July 24, 1973 C. J. FEREN ET AL 3,748,245

ELECTROCHEMICAL DEVICE FOR CHEMICAL ANALYSIS

Filed June 21, 1972

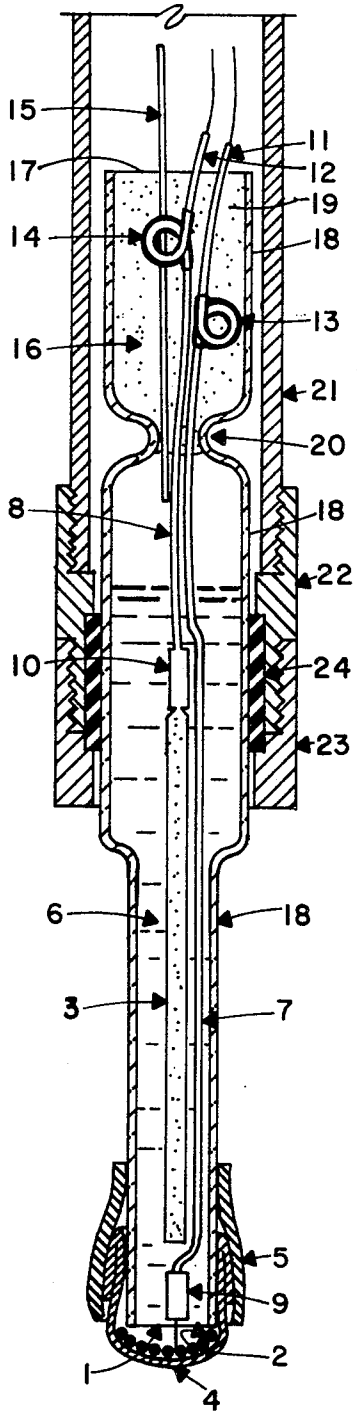


Fig. 1

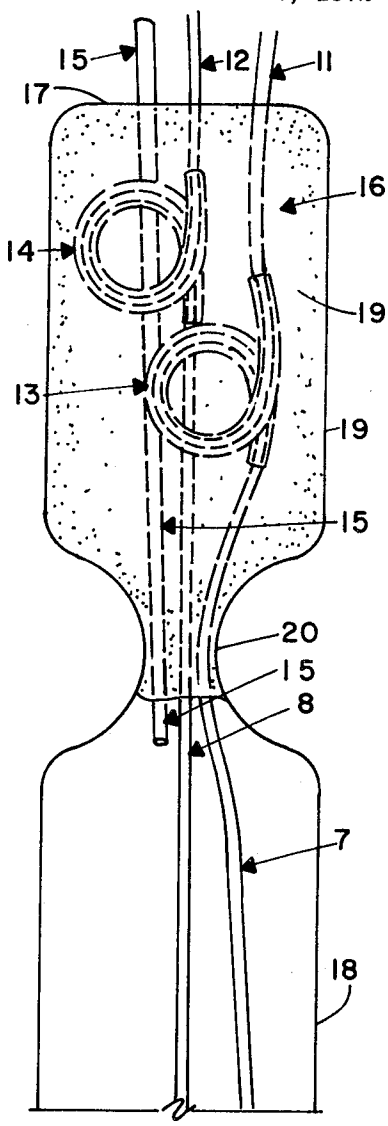


Fig. 2

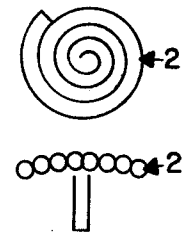


Fig. 3

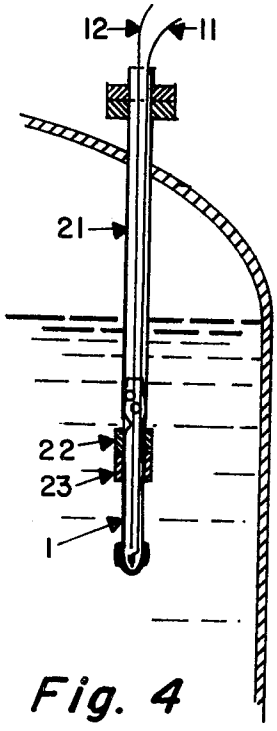


Fig. 4

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3,748,245

ELECTROCHEMICAL DEVICE FOR CHEMICAL ANALYSIS

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U.S. Cl. 204—195 P 9 Claims

ABSTRACT OF THE DISCLOSURE

Improvement to an electrochemical device for chemical analysis comprising modification of said device to provide a high temperature heat sterilizable electrolytic cell adaptable for use with a high boiling electrolyte.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to an electrochemical device for chemical analysis. More particularly, this invention relates to an improvement to the device described in U.S. Pat. No. 2,913,386.

DESCRIPTION OF THE PRIOR ART

Events leading up to the instant invention had their beginning sometime before 1923. In that year a Czech scientist named Heyrovsky announced the development of a principle of electrochemistry known as polarography. Heyrovsky's work was considered to be of such significance that he was later, in 1959, awarded the Nobel prize in Chemistry for his efforts.

Heyrovsky depended upon what is known as a "dropping mercury electrode" for his negative electrode—the cathode—in an electrolytic cell. Following Heyrovsky's announcement, it was found that a solid cathode could be utilized in place of the "dropping mercury." However, many problems were encountered from fouling of the electrode. It was then discovered that this condition could be avoided if the cathode were protected by a membrane selectively permeable to the substance to be measured.

The next significant event connected with the development of a membrane-protected electrolytic cell occurred in early 1954 when Dr. Richard V. Stow announced a device which placed both the cathode and the anode behind a selectively permeable membrane and was the forerunner of the cell to which modifications were made constituting the improvement of the instant invention.

Little reference can be offered relating to the Stow development inasmuch as Dr. Stow discussed his development in a paper presented to the American Physiology Society in Madison, Wis., in September 1954, as only an abstract of Dr. Stow's paper appeared in the American Journal of Physiology, vol. 179, p. 678 (1954).

Then came the Clark development which was disclosed in U.S. Pat. 2,913,386 noted hereinbefore.

While the Clark development was a significant and substantial advance in the art, and subsequent successful commercial exploitation of the development stands as evidence of this fact, Clark's cell had a built-in limitation in that it was not adaptable for use in installations where high temperature sterilization was required.

The improvements disclosed in the instant invention are essentially modifications to the electrochemical device disclosed and claimed by Clark.

In 1964 Johnson et al. disclosed the development of what was called a steam sterilizable probe for dissolved oxygen measurement [Johnson, M. J., Borkowsky, J. and Engblom, C., Steam Sterilizable Probes for Dissolved Oxygen Measurement, Biotechnology and Bioengineering,

vol. IX, pp. 457–468 (1964)]. Johnson's probe was a significant improvement over the Clark cell for use in applications where steam sterilization was required before the probe could be put to use. Johnson's discussion was directed primarily to the use of this device as an oxygen analyser in fermentations producing antibiotics. One of the criteria which Johnson established was that a probe which was to be steam sterilized inside a fermenter must be so constructed that the external and internal pressure of the probe was always equal. Toward that end Johnson adapted his probe to a design that utilized an upward extension of the body of the probe to a point above a vent hole in the mounting device which made it possible to equalize the pressure inside the probe with the pressure developed in the fermenter by the steam utilized for the sterilization. While this design served the purpose of equalizing the pressure between the inside of the electrochemical device and the fermenter, while the sterilization was being done, it also left an opening for materials contained in the fermentation media to enter the probe mounting and eventually find their way into the probe itself and contaminate the electrolyte, thereby rendering the probe inoperative.

In an attempt to overcome the deficiency of the Johnson probe, an effort was made to design a system that would provide for the venting of the device to the atmosphere. However, when this was done it was found that the temperature of the sterilization caused the acetate buffered electrolyte disclosed by Johnson to boil away. Consequently, the analyzer was no longer effective as an analytical cell.

Prior to the work of Johnson et al., an attempt was made to provide sealed cells which could withstand steam sterilization. These were described by Philips, et al. and Kinsey, et al. [Philips, D. H., and Johnson, M. J., Biochem. Microbiol. Technol. Eng, 3,261 (1961), and Kinsey, D. W., and Bottomly, R. A., J. Inst. Brewing, 69 164 (1963)]. Johnson, ibid. reported that in his laboratory sealed cells, on repeated sterilizations, accumulated gas bubbles and were damaged by pressure.

Accordingly, it is an object of this invention to provide an improved electrochemical device for chemical analysis which can be subjected to repeated cycles of high temperature heat sterilization and fermentation operations without impairing the precision or reliability of said device.

Another object of this invention is to provide an improved electrochemical device for chemical analysis which can be installed and operated in a vessel without the need for exposing the electrolyte in said device to the internal environment of said vessel.

Still another object of this invention is to provide an improved electrochemical device which will minimize the exposure of the electrolyte in said device to an external atmosphere.

A further object of this invention is to provide an improved electrochemical device adapted to utilize either an acetate-buffered or an alkaline electrolyte.

Yet another object of this invention is to provide a high boiling electrolyte that is adaptable for use with an improved electrochemical device when the latter is subjected to repeated cycles of high temperature heat sterilization and fermentation operations.

SUMMARY OF THE INVENTION

It has now been discovered that modifications of the electrochemical device of Clark to a high temperature heat sterilizable electrolytic cell adaptable for use with a high boiling electrolyte provides an electrolytic cell for making chemical analysis that can be utilized in conjunction with a steam sterilizable fermenter. The modi-

fications comprising the improvement to an electrochemical device for making chemical analysis comprise a lateral constriction provided in a tubular vessel for confining an electrolyte, said constriction in said vessel located above the level to which an electrolyte is filled and below the top open end of said vessel; a chamber formed in said vessel defined by the side walls, said lateral constriction and an open top end of said vessel; a combination breather-filler tube spatially disposed in said chamber, one end of said tube extending below said constriction and the other end extending above the top open end of said vessel; and a sealing means disposed in said chamber, said sealing means occupying the space in said chamber above said constriction and in adherent contact with said constriction and the side walls of said vessel, said breather-filler tube and electrical conducting means leading from the electrodes in said cell being imbedded in said sealing means, said conducting means being connectable to a means for observing variation in the electrical characteristics of said cell.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional side elevational view of an electrochemical device for use in analysing a composition to determine the quantity of a certain substance in said composition, incorporating therein the improvements of the instant invention.

FIG. 2 is a cross-sectional side elevational view of the improvements of the instant invention.

FIG. 3 comprises a plan view and a side elevational view of the cathode which is utilized in the electrochemical device.

FIG. 4 is a partial cross-sectional view showing the manner in which the electrochemical device is installed in a fermentation tank.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to the drawing, and particularly to FIG. 1 which illustrates a preferred embodiment of the improvement of this invention, there is shown an electrochemical device which provides a high temperature heat sterilizable electrolytic cell adaptable for use with a high boiling electrolyte. The improvement of this invention comprises:

(a) A lateral constriction **20** in a tubular vessel **18**, said vessel **18** having a first open end **1** and a second open end **17**, said constriction **20** located at a point in said vessel **18** above the level to which an electrolyte **6** is filled and below the second open end **17** of said vessel **18**.

(b) A chamber **19** formed in said vessel **18**, said chamber **19** defined by said constriction **20**, the side walls of said vessel **18** and the said second open end **17** of said vessel **18**.

(c) A combination breather-filler tube **15** spatially disposed in said chamber **19**, one end of said tube **15** extending below said constriction **20** and the other end of said tube **15** extending above said second open end **17** of said vessel **18**.

(d) A sealing means **16** disposed in said chamber **19**, said sealing means **16** occupying the space in said chamber **19** above said constriction **20** and in adherent contact with the side walls of said vessel **18** and said constriction **20**, said breather-filler tube **15** and electrical conducting means **7** and **8**, respectively, being embedded in said sealing means **16**.

The novel improvements of this invention perform as described and illustrated hereinafter. Inasmuch as the improvements operate in conjunction with a prior art device, it is advantageous to show the complete electrochemical device into which the modifications of this invention are incorporated.

Referring to FIG. 1, the electrochemical device is shown installed in a supporting mechanism in a manner in which the electrochemical device can be operated. A tubular vessel **18** is shown in a perspective wherein all of the elements which cooperate therewith are in place. Said vessel **18** is shown as having a first open end **1** and a second open end **17**. The first open end of vessel **18** is shown as being covered with elements that confine an electrolyte **6** above said first open end **1** of said vessel **18**. A cathode **2** is positioned across said first open end **1** of said vessel **18**. Said cathode **2** is shown in FIG. 3, both in a plan and elevational view. In a lead-silver cell the cathode is a horizontally wound spiral of a fine silver wire. In FIG. 2 a steam sterilizable selectively permeable membrane **4** covers the exterior surface of the cathode **2** and extends up to and around the side walls of said vessel **18**. It is imperative that said membrane **4** be fastened securely to the side walls of said vessel **18**. One method for fastening said membrane **4** to said vessel **18** comprises swelling a section of a silicone rubber tube **5** in chloroform until the inside diameter of said tube **5** is greater than the outside diameter of said vessel **18**. This section of swollen silicone rubber tubing **5** is then slipped over said membrane **4** and side walls of said vessel **18** and the chloroform evaporated therefrom. As the chloroform is evaporated, the silicone rubber tube **5** shrinks and forms a fastening means **5** over said membrane **4** and the outside walls of said vessel **18** thereby holding said membrane **4** in place.

Various membrane materials have been suggested by Johnson, et al., ibid. One of the preferred membrane materials for an oxygen determination is a polyfluorinated hydrocarbon polymer.

It was found in the development of this electrolytic cell that said cathode **2** must be so constructed that said electrolyte **6** can penetrate between the windings of the horizontal spiral and form a film of the electrolyte between the selectively permeable membrane **4** and the exterior surface of cathode **2**. Moreover, the lead from said cathode **2** must be so attached to an electrical conducting means **7** which extends up and through the electrolyte **6** that nothing other than the silver of the cathode is exposed to the electrolyte. In FIG. 1 the connection between the silver lead and said conducting means **7** is shown as **9**. It is of no importance what the electrical conducting means is from this point on but it is imperative that the connection and the electrical conducting means are chemically insulated from the electrolyte in order that no foreign ions are available to the electrolyte.

In this particular cell, the lead anode **3** is shown as a long strip which extends from near said first open end **1** of said vessel **18** to a position near the top level of electrolyte **6**. This design is of no significant importance to the operation of this cell but is shown in this fashion to indicate the need for the exposure of a substantial surface of the anode. Inasmuch as the chemical reaction which takes place in this electrolytic cell results in the erosion of the lead anode, it is particularly beneficial to have a large surface of said anode **3** available for the chemical reaction. The point of attachment **10** of the lead anode **3** to an electrical conducting means **8** is shown as being chemically insulated from the electrolyte. It is imperative that whatever the material of said conducting means **8** may be, it is not exposed to the electrolyte as foreign ions would be detrimental to the operation of the electrolytic cell.

Both electrical conducting means **7** from the cathode and electrical conducting means **8** from the anode must be chemically insulated from the electrolyte **6**. While many different chemically inert insulating materials can be employed, it is preferred that the insulation on conducting means **7** and **8** should be one of the poly-fluorinated hydrocarbon polymers.

The brief discussion of the electrolytic cell to this point describes a device which is old in the art. The modifications to this device which are illustrated in FIG. 2 comprise the improvement which is the substance of the instant invention. All of the elements in FIG. 2 are also incorporated into the electrolytic cell as shown in FIG. 1.

Referring to FIG. 2, there is seen a lateral constriction **20** in said vessel **18** which is a supporting means for sealing means **16** described hereinafter. Inasmuch as said vessel is generally of glass it is preferred that the supporting means provided in said vessel **18** should be a simple constriction in the glass. Said constriction **20** which here is the preferred supporting means for said sealing means can be readily formed in glass when glass is the material of construction of said vessel **18**. This constriction is formed so as to leave an opening the cross-section of which is adequate to accommodate the passage therethrough of the two electrical conducting means **7** and **8** and the combination breather-filler tube **15**. Other supporting means can be provided, such as a snugly fitting plug having an opening therein which is of a cross-sectional area sufficient to accommodate to the passage of said conducting means **7** and **8** and said combination breather-filler tube **15**. Additional supporting means will be obvious to those skilled in the art.

A combination breather-filler tube **15** is shown in FIG. 2, disposed in chamber **19** and extending to a point just below said constriction **20** and to a point above said second open end **17** of said vessel **18**. This combination breather-filler tube **15** can be of any suitable material, however, it is important that this material be chemically inert to the electrolyte utilized in the electrolytic cell. Among the materials with which tube **15** can be constructed are polypropylene, silicone rubber, gum rubber, and, preferably, a polyfluorinated hydrocarbon polymer. This breather-filler tube **15** should have an internal diameter sufficient to allow the passage therethrough of the electrolyte solution which is filled into the electrolytic cell after said cell has been assembled. This combination breather-filler tube **15** also serves the purpose of permitting an equilibration of the pressure between the electrolyte in the electrolytic cell and the outside atmosphere when the electrolytic cell is subjected to the high temperatures of sterilization. It is important that the inside diameter of said tube **15** should be held to the smallest dimension consistent with its purpose. This is necessary in order to minimize the amount of external air to which the electrolyte is exposed during the period of its operation. Traces of such gases as carbon dioxide present in external air can dissolve in the electrolyte and change the electrolytic characteristics of the cell.

A chamber **19** is formed in said vessel **18** extending from said constriction **20** up to the top edges of said second open end **17** of said vessel **18**. The combination breather-filler tube **15** and the electrical conducting means **7** and **8** extend up into and through said chamber **19**. It is preferred that said conducting means **7** and **8** are connected to second conducting means **11** and **12**, respectively, in said chamber **19**. While this is a preferred construction for reasons of economy, it is not imperative to the operation of said cell and said change of electrical conducting means does not constitute an element of the instant invention. Inasmuch as the insulation of said conducting means **7** and **8** must be of a material that is chemically inert to the electrolyte it is possible to connect said conducting means **7** and **8** to second electrical conducting means **11** and **12** on which the insulation need not be chemically inert. Therefore, said connections are shown in FIG. 2 as **13** and **14** respectively.

With said tube **15** and said connections **13** and **14** disposed in said chamber **19**, a sealing means **16** is disposed in said chamber **19**, said sealing means **16** occupying the space in said chamber above said constriction **20** and in adherent contact with said constriction **20** and the side walls of said vessel **18**, said breather-filler tube **15** and said electrical conducting means being imbedded in said sealing means **16**.

It is preferred in constructing the modifications which comprise this invention that these connections between electrical conducting means **7** and **8** and second electrical conducting means **11** and **12** should result in a one turn spiral, as shown in FIG. 2, in order that there can be a more secure anchoring of said conducting means in said sealing means **16** which is disposed in said chamber **19**.

The sealing means **16** must be chemically inert to said electrolyte **6** and have a softening point above the temperature to which the electrochemical device is exposed during heat sterilization. A number of silicone rubber base sealing compounds are available for this use and serve admirably for the purpose.

In FIG. 4, an electrolytic cell, incorporating the modifications of this invention, is shown in position in a fermenter. Said electrolytic cell is shown below the surface of the liquid media in said fermenter. Said electrolytic cell is shown installed in a mounting device which constitutes a hollow tube extending down and into the fermenter and below the surface of the liquid therein. On the end of the mounting tube **21** there is shown a mounting attachment **22** which provides for male threads at the distal end thereof and a gasket material **24**, shown in FIG. 1, is compressed against the outer walls of said vessel **18** by the pressure exerted on said gasket material **24** as the knob **23** is tightened onto the male threads of nipple **22**. This connection isolates the portion of the electrolytic cell which contains the selectively permeable membrane **4** from the atmosphere outside the fermenter and at the same time exposes said membrane **4** to the liquid media in the fermenter.

Inasmuch as fermentation operations are carried on in an environment which has been sterilized before the operation begins, and since fermentations on a commercial scale are carried out in large vessels, the most practical way to sterilize the devices which are exposed to the fermentation environment is with heat. The preferred sterilization procedure embodies the use of low pressure steam of somewhere in the neighborhood of 15 to 20 p.s.i.g. This provides a sterilization temperature in the range of from about 115° to about 121° C. An electrolytic cell as described hereinbefore, and installed in a fermenter for sterilization as described above, is exposed to the high temperature of the sterilization procedure. At least two designs can be utilized for installing an electrolytic cell in such an environment. One of these comprises installing said electrolytic cell in a mounting device which is sealed to the external atmosphere at a point between the electrolytic cell and the actual confines of the equipment to be sterilized. When this design is employed, it is imperative that a vent be provided in the mounting device which serves to equalize the pressure between the environment in which the low pressure steam is being utilized and the environment to which the electrolyte in the electrolytic cell is exposed. This is essentially the way that the Johnson, et al. device had to be mounted in order to be utilized in an environment wherein high temperature sterilization is employed. And Johnson et al., ibid., described this manner of mounting an electrolytic cell. Mounting of an electrolytic cell in this fashion for utilization in a sterilizable environment resulted in several disadvantages that made such a mounting impractical.

In the first place some of the steam which was utilized in the sterilization operation would enter the vent in the mounting device and moisture would find its way into the electrolyte solution thereby diluting said electrolyte solution and resulting in erratic operation of the electrolytic cell. This manner of mounting provides, however, the advantage that an electrolyte having a relatively low boiling point at atmospheric pressure can be utilized, because with the equalization of the pressure between the environment of the vessel being sterilized and the electrolyte environment, the boiling point of the electrolyte is raised. Such an operation can be performed where the temperature actually exceeds the boiling point of the electrolyte without any of the latter boiling away.

A distinct disadvantage of installing the electrolytic cell in the fashion discussed above was that there was always the possibility that some of the liquid media from the

fermentation process would get into the vent, find its way into the electrolyte of the electrolytic cell and consequently poison the cell. This occurred frequently, and it was found that such an installation often resulted in the electrolytic cell failing during the course of the fermentation operation. Sealing the electrolyte in the electrolytic cell, as discussed by Johnson et al., ibid., did not serve to solve this problem as the electrolyte would become exhausted long before the anode was no longer utilizable and as a consequence the life of the cell was substantially diminished.

The modifications comprising the improvement of the instant invention made it possible to utilize the principle of the Clark electrochemical device in a high temperature heat sterilizable environment, because the internal elements of the electrolytic cell were isolated from the environment of the fermentation vessel, not only during the time when heat and pressure were being applied to the exposed external surfaces of the electrolytic cell in the form of the steam sterilization, but during the course of the fermentation operation as well. Inasmuch as it is essential to minimize the exposure of the electrolyte to an external atmosphere, the modifications constituting the improvement of this invention offer the means by which the fluctuations in the vapor pressure of the electrolyte, occurring with repeated cycles of high temperature sterilization and fermentation operations, can be accommodated with the least exposure of said electrolyte to such an atmosphere.

Coincidentally, with the development of modifications to provide for a minimum exposure to an external atmosphere, a high boiling electrolyte was developed that is adaptable for use with the improved electrochemical device of this invention. The development of this high boiling electrolyte provided an element which could be utilized in cooperation with the design of the Clark device that did not require the application of a pressure equalizing environment to the electrolyte during the high temperature heat sterilization operation.

Johnson et al., ibid., discussed the adaptation of both alkaline and acetate buffer electrolytes to a lead-silver cell such as that described hereinbefore. Johnson observed that when alkaline electrolytes were utilized in an environment in which fermentations were being conducted, the high carbon dioxide content present resulted in a rapid poisoning of the electrolyte and consequently rendered such electrolyte inoperative. This, of course, was due to the manner in which Johnson's cell was installed, to wit, with a vent in the mounting device exposing the electrolyte solution to the environment of the fermentation operation. With the development of the modifications to the Clark cell which comprise the improvement constituting the present invention, there is no longer an exposure of the electrolyte to the high carbon dioxide concentration in the fermentation environment. Therefore, it is possible to employ alkaline electrolytes in the electrolytic device described hereinbefore. In order that alkaline electrolytes can be operative in this modified electrolytic cell it is imperative that such electrolytes have a boiling point wherein the vapor pressure of the electrolyte is below that of the atmosphere at the temperature of the sterilization. In which case, the electrolyte will not boil away at the temperature of the sterilization.

A novel high boiling electrolyte was developed that is adaptable for use with the modified Clark electrochemical device described hereinbefore. This novel electrolyte comprises a solution of propionic acid, sodium hydroxide, and glycerol. It was found that a suitable high boiling electrolyte adaptable for use with said cell could be comprised, in each 100 ml., of from about 36 to about 60 grams of propionic acid, from about 1.5 to about 2.5 grams of sodium hydroxide, and sufficient glycerol to make the 100 ml. Such an electrolyte has a boiling point at 135° C. or above. A preferred composition for a high boiling electrolyte is comprised of about 48 grams propionic acid, about 2 grams of sodium hydroxide and sufficient glycerol to make 100 ml. This preferred electrolyte has a boiling point at about 138° C.

The improved electrolytic cell of this invention, utilizing a high boiling electrolyte of a composition described above, can be installed in a fermentation tank in a fashion such as that discussed hereinbefore, and operated through repeated cycles of sterilization and fermentation, without impairing the accuracy and reliability of such a cell. Moreover, when the electrolyte in such a cell becomes exhausted it is convenient to remove the cell from its mounting and drain the electrolyte therefrom. The cell can then be recharged with new electrolyte and returned to its position in the fermenter and again subjected to repeated cycles of sterilization and fermentation. Inasmuch as the silver cathode is not consumed in the operation of the cell, there is no life span limitation due to an erosion of the silver. On the other hand the lead anode is consumed in the operation of the cell and, barring unforeseen accidents which destroy the cell, the device can be utilized through continuous operation until the lead anode is consumed to the point where the electrical characteristics of the cell are no longer reliable.

The electrolytic cell which forms the basis for the modifications constituting the improvements of this invention can be operated as either a galvanic cell, commonly called a self-generating cell, or a polarographic cell. When this cell is operated as a polarographic cell, an external source of electrical current is applied to the cell and measured across a resistance. Then in operation, the cell develops an additional potential of its own which is added to the electrical potential being applied thereto and the sum of the two is read on an instrument which can be calibrated to indicate the actual amount of electromotive force being generated by the electrolytic cell.

In either event, the electromotive force which is generated by the cell is calibrated against the concentration of whatever substance it is desired to measure in the composition to which the electrolytic cell is exposed. In a highly useful application of this modified electrochemical device, the oxygen content of a fermentation media can be determined. Oxygen present in the fermentation media passes through the selectively permeable membrane and contacts the silver cathode. A series of chemical reactions are initiated which result in the development of an electromotive force across the cell. The rate of the chemical reaction controls the quantum of the electromotive force produced; the faster the rate of the chemical reaction the greater the electromotive force produced. Inasmuch as the rate of the chemical reaction is controlled by the rate of the oxygen permeation of the selectively permeable membrane, the amount of oxygen present in the fermentation media is measurable as a direct correlation with the quantum of electromotive force produced by the electrolytic cell.

The modifications to the Clark electrochemical device, which constitute the improvement of this invention, have resulted in an electrolytic cell which can be subjected to repeated alternate cycles of high temperature heat sterilization and fermentation without impairing the precision or reliability of the electrochemical device. Electrolytic cells, which heretofore could be utilized through only a few alternate cycles of sterilization and fermentation, or which did not survive even one complete cycle due to poisoning of the electrolyte, are now available which can be utilized continuously until such time as the lead anode has been consumed to the point where the electrical characteristics of the cell are no longer consistent.

What is claimed is:

1. In an electrolytic cell for use in analyzing a composition to determine the quantity of a certain substance in said composition, said cell comprising:

(1) an anode,

(2) a cathode,

(3) means for supporting said anode and said cathode in a fixed space relationship,

(4) a tubular vessel for confining an electrolyte in electrical current carrying contact with said anode and said cathode, said vessel having a first and a second open end,

(5) a selectively permeable membrane covering said cathode covering and enclosing said first open end of said vessel to physically separate and electrically insulate said cathode, said anode, and said electrolyte from the composition being analyzed, said membrane being permeable to the substance in said composition the quantity of which it is desired to determine, said substance being reactable with said electrolyte to alter the electrical characteristics of said cell, said membrane being impermeable to all other constituents of said composition reactable with said electrolyte,

(6) electrical conducting means connected to said anode and said cathode, said conducting means chemically insulated from said electrolyte, and

(7) means for observing variations in the electrical characteristics of the cell connected to said conducting means;

the improvement comprising modifications of said cell to provide a high temperature heat sterilizable electrolytic cell adaptable for use with a high boiling electrolyte wherein:

(a) a constriction is provided in said tubular vessel for confining an electrolyte, said constriction located at a point in said vessel above the level to which said electrolyte is filled and below the top edge of said second open end of said vessel,

(b) a chamber is formed in said vessel defined by the side walls and said second open end of said vessel and said constriction,

(c) a combination breather-filler tube is spatially disposed in said chamber, one end of said tube extending below said constriction and the other end extending above the top edge of said second open end of said vessel, and

(d) a sealing means is disposed in said chamber, said sealing means occupying the space in the said chamber above said constriction and in adherent contact with said constriction and the side walls of said vessel, said breather-filler tube and electrical conducting means leading from the electrodes in said cell being imbedded in said sealing means, said conducting means being connectable to a means for observing variations in the electrical characteristics of said cell.

2. The electrolytic cell as defined in claim 1 wherein the constriction comprises a venturi-like shape formed in said vessel, said constriction having an inside open cross-sectional area large enough for said breather-filler tube and said electrical conducting means to pass therethrough.

3. The electrolytic cell as defined in claim 1 wherein the constriction comprises a snug fitting plug inserted into said vessel, said plug having an opening therein with a cross-sectional area large enough for said breather-filler tube and said electrical conducting means to pass therethrough.

4. The electrolytic cell as defined in claim 3 wherein said plug is comprised of a material which is chemically inert to said electrolyte.

5. The electrolytic cell as defined in claim 4 wherein said plug is comprised of a polyfluorinated hydrocarbon polymer.

6. The electrolytic cell as defined in claim 1 wherein the chamber formed in said vessel has a longitudinal dimension to lateral dimension of from a ratio of about 0.5 to 1 to 10 to 1.

7. The electrolytic cell as defined in claim 6 wherein said chamber has a longitudinal dimension to lateral dimension ratio of about 3 to 1.

8. The electrolytic cell as defined in claim 1 wherein said tube is comprised of a polyfluorinated hydrocarbon polymer.

9. The electrolytic cell as defined in claim 1 wherein said sealing means is a compounded silicon rubber-based sealing compound.

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GERALD L. KAPLAN, Primary Examiner

U.S. Cl. X.R.

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