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G. BERGSON ET AL

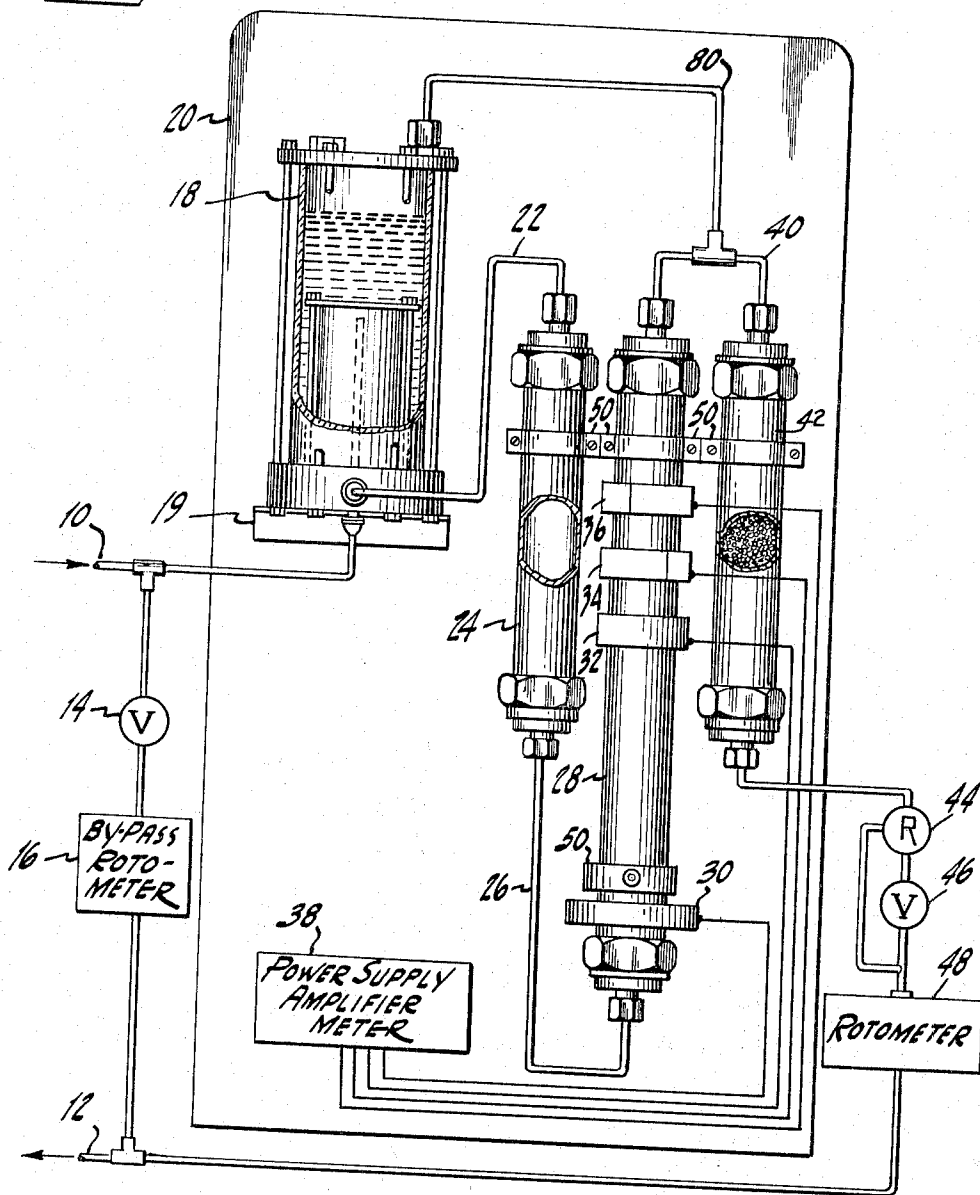
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OXYGEN ANALYZER

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Fig. 1.



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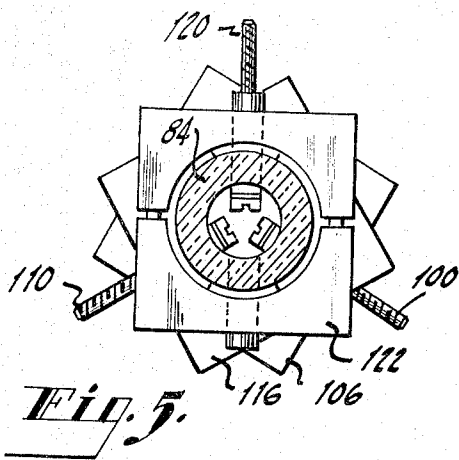
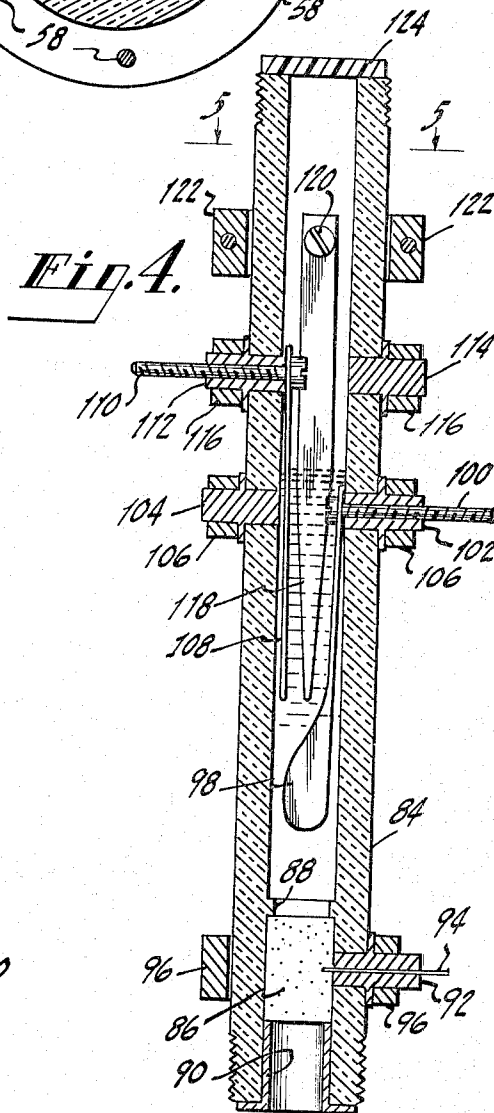
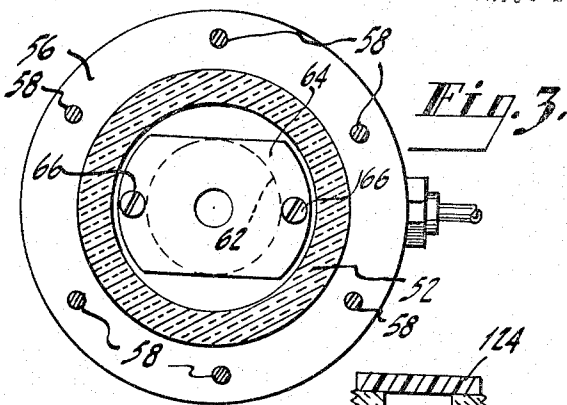
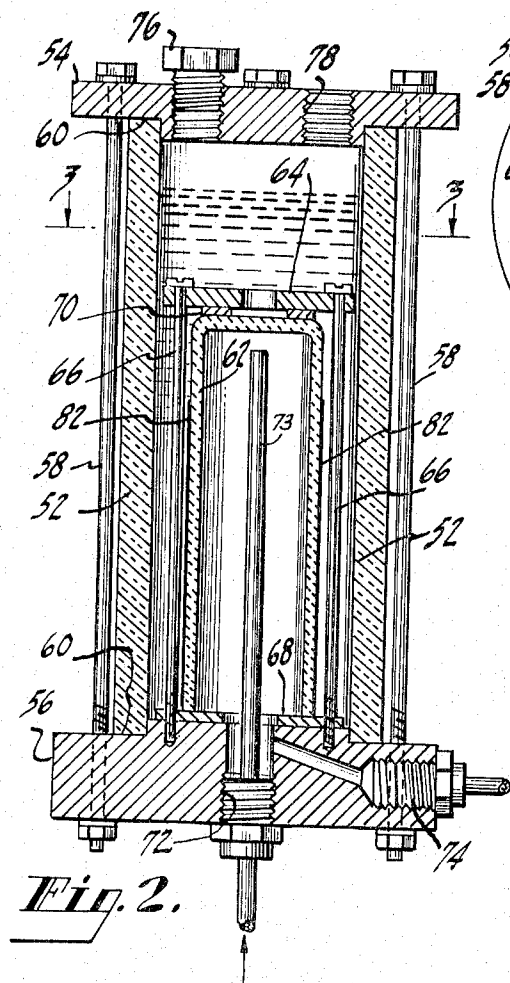
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3 Sheets-Sheet 2



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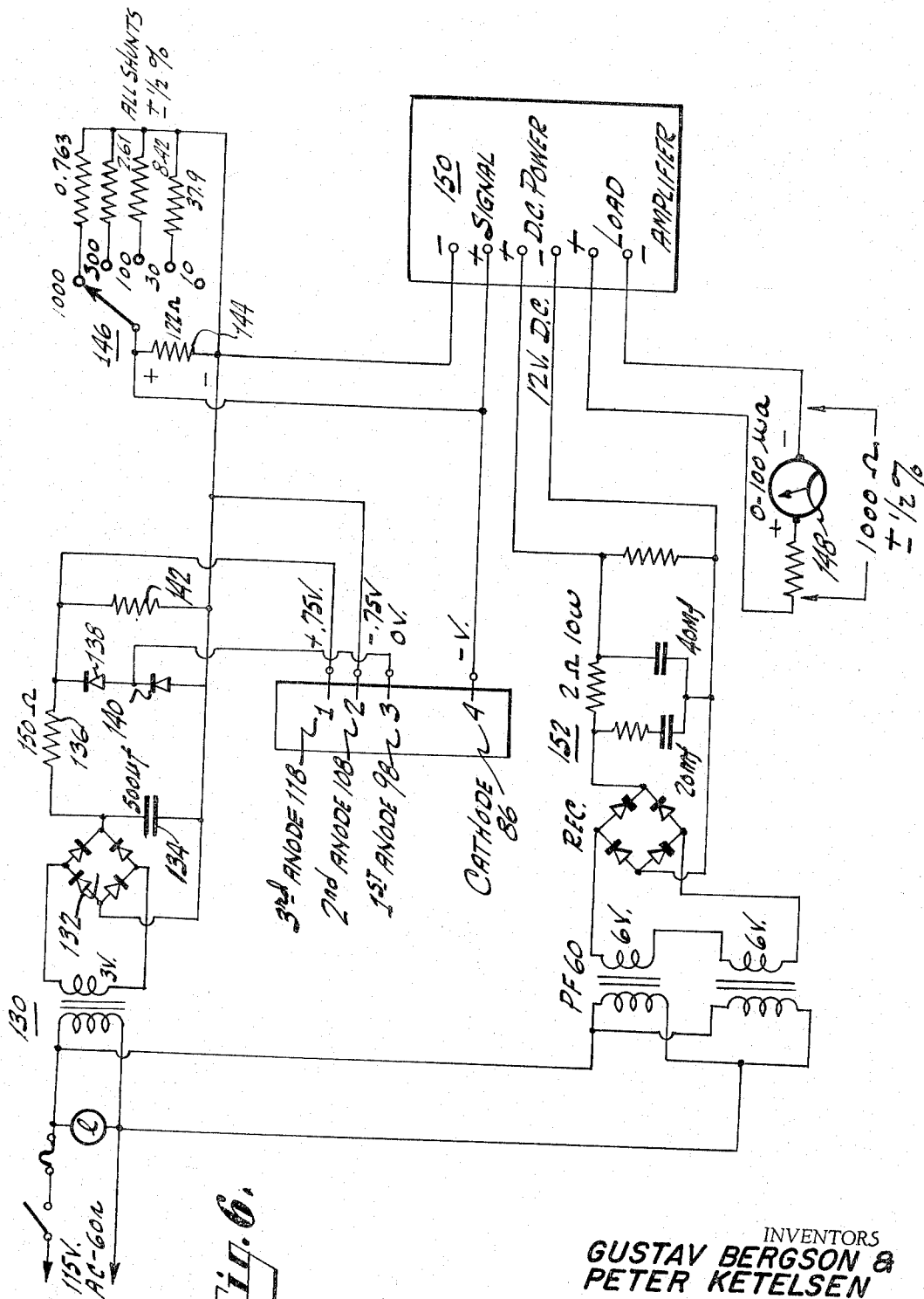


Fig. 6.

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OXYGEN ANALYZER

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1 Claim. (Cl. 204-195)

This invention relates to gas analyzing systems, and more particularly to improved systems for the electrolytic measurement of the oxygen concentration of a gas stream.

Electrolytic oxygen analyzers have heretofore been proposed which depend for operation on the quantitative reduction of gaseous oxygen with the concurrent liberation of electrons which constitute a flow of current, the magnitude of which is related to the oxygen concentration in accordance with Faraday's Law of Electrolysis. Briefly, a gas stream to be analyzed is passed at a known rate of flow through a cathode which is in contact with an aqueous electrolyte solution. The cell is operated at potentials which do not cause dissociation of the electrolyte while maintaining the potential of the cathode with respect to the electrolyte solution sufficiently negative, with respect to that which would correspond to equilibrium, to insure essentially quantitative operation where in each atom of the oxygen molecule gives up two electrons while going over into the hydroxyl ion at the cathode. In similar fashion, the principal electrolysis anode is maintained at a potential sufficiently positive with respect to that which would determine equilibrium to reverse the cathode action. Experience shows that these potentials can be maintained without violating the requirement with regard to the cell electrolyte.

The anode and cathode elements must be of a type which are not subject to rapid attack by the electrolyte solution. For example, with a potassium hydroxide (KOH) solution, the cathode material may comprise silver or copper, and the principal anode may comprise a stainless steel container for the cell. A third electrode included in known quantitative oxygen analyzers consists of a large rod which may be cadmium. The hydroxyl ions formed at the cathode are released as molecular oxygen at the stainless steel anode, and are carried out of the system by the gas stream bubbling through the electrolyte. Quantitative oxygen analyzer systems heretofore available have been bulky and expensive in construction. One reason is that the known oxygen analyzer cells per se are quite large and difficult to build. Another reason is that the gas flow regulating apparatus of prior systems must be constructed of materials which resist attack by the corrosive electrolyte solution picked up in vapor and molecular form by the gas stream.

As a result of their resultant size and weight, existing oxygen analyzing systems are considered to be semi-permanent installations, and are not well adapted for use in applications requiring a portable instrument. In addition to the foregoing problems with respect to size, weight and expense, it has been found that the hold up time of existing apparatus is sometimes undesirably long. The hold up time of the instrument is the time it takes the instrument to indicate changes in the oxygen content of a gas stream from the time the gas stream with the changed oxygen content is introduced into the system.

It is an object of this invention to provide an improved oxygen analyzer.

A further object of this invention is to provide an improved oxygen analyzer which is relatively small, light in weight and inexpensive as compared to known types of oxygen analyzers, so as to be useful as a portable apparatus.

Another object of this invention is to provide an improved oxygen analyzer cell.

Still another object of this invention is to provide an improved oxygen analyzing system having a relatively small hold up time as compared to known types of oxygen analyzers.

An oxygen analyzing system embodying the invention includes a gas inlet port for admission of the gas stream whose oxygen content is to be measured. The gas stream is passed through a novel wetter cell, the function of which will be described hereinafter, to an electrolytic oxygen analyzer cell. If desired, a trap may be provided between the wetter cell and the oxygen analyzer cell so that interruption of the pressure of the gas stream prevents a back-flow of the electrolyte solution from the oxygen analyzer cell into the wetter cell and, subsequently, the gas inlet lines.

After the gas has passed through the oxygen analyzer cell, it is passed through a neutralizer. The gas outlet port from the oxygen analyzer includes a porous filter so that the electrolyte in mist form, which is picked up by the gas stream, is blocked and returned to the analyzer cell. That portion of the electrolyte which is picked up in molecular form is removed in the neutralizer. The neutralizer cell comprises a housing containing a material which is highly reactive with the electrolyte, and hence readily combines with that portion of the electrolyte in molecular form to insure its substantially complete removal from the gas stream. By way of example, where the electrolyte solution is KOH, pellets of aluminum may be placed in the neutralizer cell to provide a large surface contact area for the gas stream as it passes therethrough. It has been found that virtually all of the KOH in molecular form reacts with the aluminum and is hence removed from the gas stream.

As a consequence of removing the corrosive electrolyte material from the gas stream, the gas flow rate controlling and measuring means such as the differential pressure regulator, valves, rotometers etc., may comprise items which are relatively inexpensive as compared to components which must be built in a manner to resist the corrosive effects of the electrolyte. Thus, the neutralizer cell contributes substantially to the reduction in cost of the oxygen analyzer system of the invention as compared to prior systems.

Another aspect of the invention pertains to the oxygen analyzer cell per se which is relatively small in size, light in weight and inexpensive in construction as compared to prior known types of oxygen analyzer cells. The oxygen analyzer cell of the invention is housed in a light weight transparent tubular casing of lucite or the like, and includes a porous active cathode, and three anode electrodes. The cathode, which may, for example be comprised of porous silver, is mounted near the end of the casing which comprises the gas inlet port. A first anode which extends to a position in the vicinity of the cathode provides a dual function of shielding the cathode from impurities and establishing the solution potential. The first anode may, for example, comprise a loop of cadmium which has a substantial surface area confronting the cathode. A third anode electrode is provided for completing the reaction process. The third or principal anode comprises a strip of material such as stainless steel, and has a surface area of the order of that of the cathode.

A second anode electrode included in the tube comprises an impurity collector. As described in Flook et al. 2,898,282, minor amounts of reducible impurities are contained in the electrolyte solution some of which result from the gradual corrosive action of the electrolyte on the third anode electrode. These impurities tend to coat the first anode causing ultimate cell failure. In prior cells this electrode was made relatively large to de-

lay such failure at the expense of size and weight. This problem is reduced in the cell of the invention by the second electrode which is maintained at a potential to attract the impurity ions and thereby prevent undesirable coating of the first anode. Since the problems caused by the impurity coating is substantially obviated by the second anode operation, the first anode can be made relatively small in size, thus substantially reducing the size, weight and cost of the analyzer cell. The resultant smaller size of the analyzer cell permits the practical use of transparent, easily machinable materials as a container for the electrolyte and electrodes, thereby permitting instantaneous operational checks on the state of the measuring equipment as it relates to proper maintenance of replaceable materials. In addition, the smaller analyzer cell permits shorter lengths of tubing to be used in connecting the cell with the remainder of the system, thus further contributing to overall system size reduction.

An appropriate electrolyte, such as a KOH solution, is introduced into the cell, and appropriate potentials are applied to the electrodes as will hereinafter be described.

Another important aspect of the invention comprises the novel wetter cell through which the gas passes prior to its admission to the analyzer cell. The purpose of the wetter cell is to establish the moisture content of the gas stream at an equilibrium condition for the temperature of the electrolyte solution in the analyzer cell. Thus, the gas stream in passing through the electrolyte gives up as much moisture as it absorbs, and hence does not tend to remove moisture from the electrolyte. The wetter cell of the invention comprises a porous ceramic or like enclosure immersed in an aqueous solution in a manner that the solution can get into the enclosure only by diffusion through the porous walls thereof. The gas stream is admitted into the enclosure, and picks up moisture by circulating in contact with the wet inner walls thereof. This wetter cell construction keeps the hold-up time of the analyzing system short because the gas stream does not bubble through the solution, and hence oxygen in the gas stream is not picked up by the solution. Thus if the oxygen content in the stream is changed, the time required to establish an equilibrium condition due to oxygen being absorbed or given up by the solution is very short.

To prevent the solution from collecting inside the enclosure, the diffusion rate of the solution through the porous material may be controlled by coating a portion of the solution contacting surface of the porous enclosure with a non-porous blocking material. As will be described more fully hereinafter, the rate of diffusion of the solution through the porous material is automatically controlled as a function of the amount of moisture picked up by the gas stream with the rate being such as to prevent accumulation of the solution in the interior of the enclosure.

The novel features which are considered to be characteristic of this invention as well as additional objects and advantages thereof will be understood more clearly when read in connection with the accompanying drawings in which:

FIGURE 1 is a diagrammatic and block diagram of an oxygen analyzing system embodying the invention;

FIGURE 2 is an elevational view, in section, of a wetter cell embodying one aspect of the invention;

FIGURE 3 is a sectional view of the wetter cell taken on section lines 3—3 of FIGURE 2;

FIGURE 4 is an elevational view, in section, of an oxygen analyzer cell embodying another aspect of the invention;

FIGURE 5 is a top view of the oxygen analyzer cell shown in FIGURE 4; and

FIGURE 6 is a schematic circuit diagram of the power supply and metering circuits for connection to the oxygen analyzer cell.

Referring to FIGURE 1, the oxygen analyzing system of the invention comprises an inlet port 10 to which gas under pressure is admitted. The inlet port 10 is connected to the gas outlet port 12 by a bypass valve 14 and a bypass rotometer 16. Gas from the inlet port 10 is directed through a wetter cell 18 which is mounted on a bracket 19 affixed to a chassis 20 for the apparatus. From the wetter cell 18, the gas is passed through a tube 22 to a trap 24 which comprises a tube of transparent material of sufficient volume to prevent back-flow of fluids into the wetter cell 18. The outlet side of the trap 24 is coupled by a pipe 26 to an oxygen analyzer or electrolytic cell 28.

The analyzer cell 28 includes a cathode mounting block and terminal 30, and first, second and third anode mounting blocks and terminals 32, 34 and 36 respectively. The respective mounting blocks and terminals are connected to a power supply, amplifier and metering circuit 38.

After the gas has passed through the analyzer cell 28 it is directed through a tube 40 to a neutralizer cell 42. The neutralizer cell is filled with a material which reacts with the electrolyte solution, so that any of the electrolyte solution picked up by the gas stream is removed before the gas leaves the neutralizer cell. In the present case, where the electrolyte used in the analyzer cell 28 is KOH, the neutralizer cell is filled with aluminum pellets which provide a large surface area to the gas passing there-through. The neutralizer cell housing comprises a transparent tube of lucite or the like so the visual condition of the neutralizer material may be easily ascertained by the operator of the apparatus.

The gas flow rate through the analyzer cell 28 is controlled by a differential pressure regulator 44 and a valve 46, connected in series, to the outlet port of the neutralizer cell 42. The gas flow rate is indicated by a rotometer 48 connected in the gas line between the valve 46 and the outlet port 12.

The trap 24, analyzer cell 28 and neutralizer cell 42 are mounted on the apparatus chassis 20 by suitable mounting means indicated in FIGURE 1 by the blocks 50. The lower end of the analyzer cell is preferably well below that of the wetter cell 18 to minimize the risk of back-flow of the electrolyte from the analyzer cell 28 when the inlet port 10 pressure is removed. Any back pressure tending to produce electrolyte back-flow may be further dissipated by using capillary tubing for the tubes 22 and 26.

The wetter cell 18 which is shown in greater detail in FIGURES 2 and 3, comprises a transparent tubular casing 52 clamped between a pair of end plates 54 and 56 by a plurality of bolts 58. Suitable gaskets 60 are provided between the casing 52 and the end plates to provide a water tight enclosure. A porous ceramic cup 62 is positioned within the water tight enclosure, and clamped between a clamp plate 64 and the bottom plate 56 by a plurality of bolts 66. A gasket 68 is provided at the lower end of the cup 62 to provide a further water tight enclosure within the cup. A gasket 70 is provided between the top of the cup 62 and the clamp plate 64 to prevent damage to the cup when the bolts 66 are tightened.

A gas inlet opening 72 for connection with the inlet port 10, and a gas outlet opening 74 for connection with the pipe 22 (FIGURE 1) are provided in the bottom plate 56. A tube 73 conveys the gas admitted to the wetter cell well up in the cup 62 to insure that the gas circulates against the wet walls of the cup. The top plate includes a threaded opening for receiving a fill plug 76. Water or other suitable solution is admitted to the wetter through this opening. A second threaded opening 78 is provided in the top plate 54 for communication through a tube 80 to the tube 40 of FIGURE 1. The tube 80 provides a feedback connection which tends to maintain a pressure differential between the portion of the enclosure holding the water, and that inside the cup 62 at a value which varies as a function of the gas flow rate.

Diffusion of the water through the porous walls of the cup 62 wets the inner surface thereof. The gas circulating through the cup picks up the water to establish an equilibrium condition for the temperature at which the process operates. By wetting the gas in this manner, the amount of oxygen picked up and held by the water is very small as compared to a wetter where the gas is bubbled directly through the water. Thus, the hold-up time of the system is very low.

To prevent the water from diffusing through the porous cup 62 at a rate which would cause water to collect inside the cup and block the gas line tubes, a portion of the cup is covered with a water barrier 82 of lucite or the like. Water diffuses through the porous material at a rate determined by the difference in wetness between the inside and outside surfaces thereof. As a result of this feature, the area of the porous material of the cup exposed to the water, and the average head of water is selected in a non-critical fashion to provide substantially no excess flow of the water which would cause collection at the bottom of the cup 62.

When the gas passing through the system picks up relatively large amounts of the water and thereby tends to dry out the inside surface of the cup 62, the difference in wetness between the inside and outside of the cup increases the rate of diffusion of the water. When relatively little water is picked up by the gas stream, this differential wetness is quite low thereby reducing the diffusion rate. The portion of the cup 62 covered by the water barrier 82 provides a reservoir for any excess water which may diffuse through the exposed portions of the porous cup 62 and the system is self-stabilizing.

The improved oxygen analyzer cell 28 is shown in greater detail in FIGURES 4 and 5. The analyzer cell 28 includes a tubular casing 84 of transparent material such as lucite. The top and bottom portions of the casing 84 are threaded to receive gas tube fittings shown in FIGURE 1. A porous silver cathode 86 is seated between a boss 88 formed in the casing 84 and a bushing 90 inserted into the end of the casing. A Teflon plug 92 having a central conductive probe 94 extends through an aperture in the casing 84 so that the probe 94 contacts the silver cathode 86. The plug 92 is retained in position by a two piece clamp 96 fastened about the casing 84. The tube 26 (FIGURE 1) is coupled by a suitable fitting to admit gas to the bottom of the casing 84.

A first anode electrode 98 comprising a strap of cadmium bent into a loop shaped configuration is positioned adjacent, but spaced from the cathode 86. The first anode 98, which is shown in side view, provides a substantial surface area in confrontation to the cathode. The first anode is held in position by a screw 100 which passes through a Teflon plug 102 in the wall of the casing. The screw 100 is inserted through an aperture in the casing 84 blocked by a plug 104. The plugs 102 and 104 are retained in position by a two piece clamp 106 which is fastened about the casing 84.

A second anode or impurity collector 108 comprises a strip of cadmium extending to a position above the first anode 98. The second anode 108 is held in position by a screw 110 passing through a Teflon plug 112 in the wall of the casing 84. The screw 110 is inserted through an aperture in the casing 84 blocked by a plug 114. The plugs 112 and 114 are retained in position by a two piece clamp 116 which is fastened about the casing 84.

A third anode 118 comprises a stainless steel strip extending down into the casing 84 about the same distance as the second anode 108. The third anode is supported by a screw 120 extending through a plug in the manner described above, and held in position by a clamp 122. Each of the plugs extending through the various apertures in the casing 84 have a lip portion which is pressed by the respective clamps against the body of the casing 84 to provide a water tight seal.

The casing 84 is filled with electrolyte, such as a solu-

tion of KOH, to a level to contact all electrodes. As shown in the drawings, the electrolyte extends to a level just above the clamp 106. The gas stream in passing through the analyzer cell tends to pick up the electrolyte in mist and molecular form. A porous Teflon filter 124 removes that portion of the electrolyte which is picked up in mist form, and that portion picked up in molecular form is removed by the neutralizer 42 of FIGURE 1. The electrolyte in mist form blocked by the filter 124 drains back into the analyzer cell 28.

Electrical connections are made to the various electrodes by connection to the screws 120, 110 and 100 and the probe 94. The electrical circuit for the analyzer is shown in FIGURE 6.

Power from an alternating current source is applied through a transformer 130 to a bridge rectifier 132 to develop a direct voltage. The direct voltage is filtered by a capacitor 134 and a resistor 136, and applied across a pair of series connected zener diodes 138 and 140. A resistor 142 is connected in parallel with the series connected zener diodes. The total voltage appearing across the diodes 138 and 140 is about 1.5 volts.

The cathode of the diode 138 is connected to the third anode 118, and the junction of the diodes 138 and 140 is connected to the first anode 98. The anode of the diode 140, which is at the most negative potential is connected to the second anode 108. The cathode 86 of the analyzer cell is connected to the anode of diode 140 through a resistor 144. As shown in the drawings, any one of several resistors may be connected in parallel with the resistor 144 by a switch 146. The various resistors provide meter range shunts.

The current flowing through the oxygen analyzer cell is indicated on a meter 148. The meter 148 is driven by a low input impedance amplifier 150, which may, by way of example, comprise a magnetic amplifier. Direct voltage for energizing the amplifier 150 is derived from a full wave rectifier circuit 152. The amplifier 150 has an input impedance which is sufficiently low so that changes in the setting of the range switch 146 does not produce a sufficient change in voltage drop across the resistor 144 to affect the electrolysis action in the analyzer cell. Hence the time required for the electrodes to reach a new equilibrium condition is very short as the meter range switch 146 is moved from position to position.

The relatively inactive first anode 98 has a sufficient area to establish the relative potential of the electrolyte in the analyzer cell which potential will be considered as a reference. The anode 98 thus provides a potential base, tied closely to the electrolyte potential, from which other electrode potentials are established.

The second anode 108 is at a potential of about -0.75 volt relative to the first anode 98 and the electrolyte. Similarly, the cathode is about -0.65 volt relative to the first anode 98 and the electrolyte, that is -0.75 volt less the slight voltage drop across the resistor 144. The third anode 118 is at about +0.75 volt positive relative to the first anode 98 and the electrolyte. These voltages are properly located with respect to the known equilibrium potential to permit the quantitative oxygen-reduction process. At the same time the dissociation potential of water, approximately 1.7 volts, is never reached. Oxygen bubbled in contact with the cathode 86 and the electrolyte produces negative hydroxyl ions requiring electrons from the cathode 86. The negative hydroxyl ions are removed from the vicinity of the cathode by the sample gas, and the excess solution negative ions are removed by the re-establishment of equilibrium due to hydroxyl ion reaction at the third anode with simultaneous release of electrons and oxygen. The electron current flow between the cathode 86 and the third anode 118 is a function of the amount of oxygen in the gas stream determined by Faraday's Law of Electrolysis. The electron current flowing between the anode and cathode passes through the resistor

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144 and meter shunts therefor which are across the input terminals of the amplifier 150. Thus the magnitude of electron current determines the signal input level to the amplifier 150 and the reading of the meter 148.

Impurities in the anodes and in the electrolyte solution produce positive ions. To prevent these ions from being attracted to the first anode or cathode and coating it with the impurities, the second anode electrode 108 is provided with the most negative potential. In addition, since the electrode 108 is physically positioned much closer to the other anodes than is the cathode, any ions released by the anodes are more strongly affected by the field of the second anode 108, and are attracted thereto. The second anode 108, in reducing the coating of the first anode 98, extends the effective useful life of this electrode. As a result, the size of the anode 108 may be relatively small as compared to corresponding anodes in known oxygen analyzer cells which provide an equivalent useful life. As a result the overall size, weight and cost of the oxygen analyzer all embodying the invention is materially reduced.

By virtue of the construction described, the oxygen analyzer cell of the invention is considerably smaller, lighter and less expensive than prior known cells for effecting the same result. In addition the present analyzer cell has been found to be highly accurate and reliable in operation, and well adapted for portable or semi-permanent applications.

What is claimed is:

Apparatus for the quantitative analysis of oxygen in a flowing gas stream comprising in combination of an electrolytic cell provided with a porous cathode element, an anode element in contact with an aqueous electrolyte solution, a gas sample supplying conduit opening adjacent said cathode element to direct said flowing gas stream through said porous cathode element into intimate contact therewith and with said electrolyte solution to thereby effect electrolytic reduction of the oxygen in said flowing gas

stream, a gas stream outlet port for said electrolytic cell, a wetter for humidifying said flowing gas stream to substantially an equilibrium condition for the temperature of said electrolyte prior to the time said gas stream is applied to said conduit opening, said wetter comprising an enclosure for an aqueous solution, means providing a porous container within said enclosure, said porous container sealed to prevent the entry therein of said solution except by diffusion of the solution through the porous walls thereof, gas inlet and outlet means into said container wherein gas admitted to said container through said gas inlet means is exposed to that portion of said solution which has diffused to the inner wall of said porous container, means for coupling the gas outlet means of said wetter to said conduit opening, and a gas stream feedback connection communicating between the gas stream outlet port for said electrolytic cell and the interior of said enclosure.

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