

Aug. 4, 1959

W. M. FLOOK, JR., ET AL
ELECTROLYTIC OXYGEN ANALYSIS

2,898,282

Filed June 20, 1956

3 Sheets-Sheet 1

FIG. 1

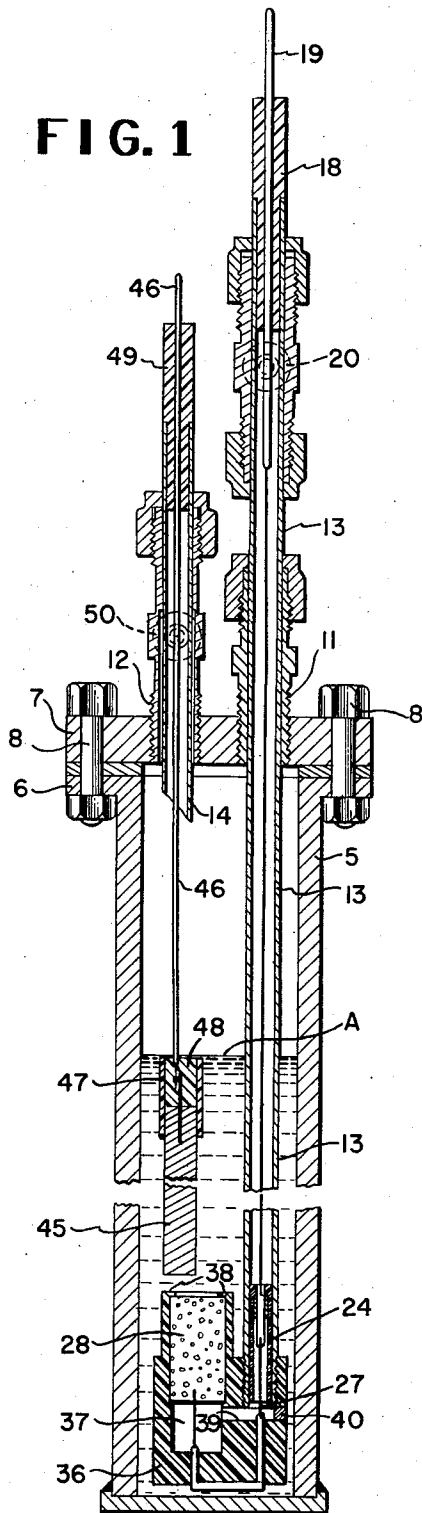


FIG. 2

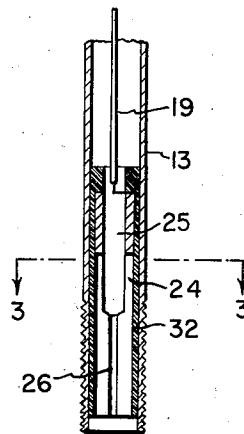
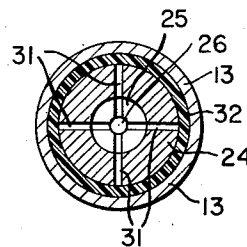


FIG. 3



INVENTORS

WILLIAM M. FLOOK, JR.
and FREDERICK A. KEIDEL

BY *Harry J. McCarley*
ATTORNEY

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3 Sheets-Sheet 2

FIG. 4

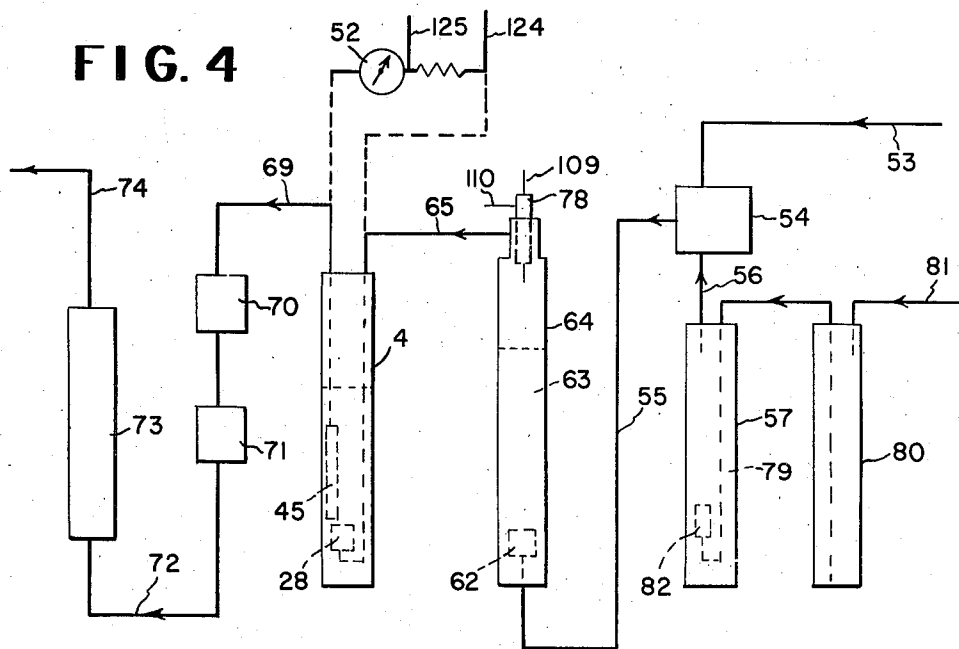
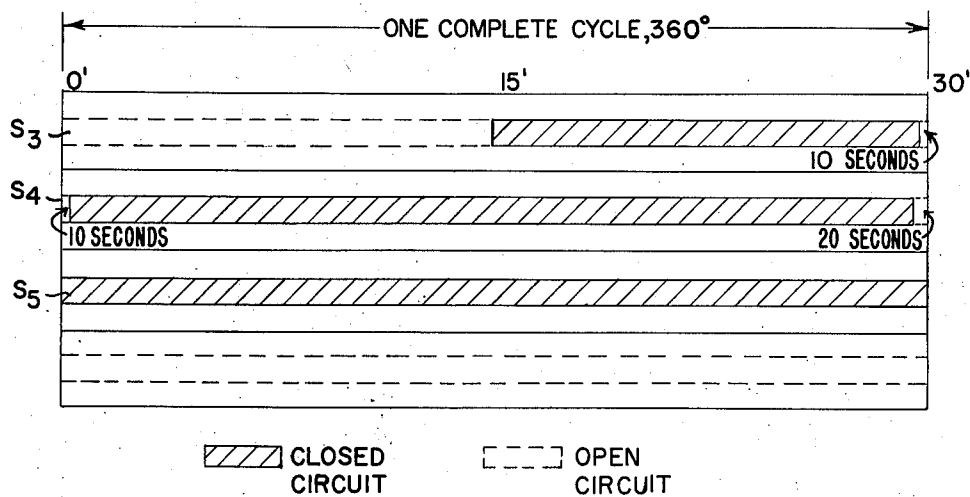


FIG. 6



INVENTORS

WILLIAM M. FLOOK, JR.
and FREDERICK A. KEIDEL

BY

Harry J. McCauley

ATTORNEY

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2,898,282

ELECTROLYTIC OXYGEN ANALYSIS

William M. Flook, Jr., Greenville, and Frederick A. Keidel, Wilmington, Del., assignors to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

Application June 20, 1956, Serial No. 592,674

4 Claims. (Cl. 204—195)

This invention relates to improvements in electrolytic analysis and particularly to a method and apparatus for the analysis of low or medium concentrations of oxygen in a gaseous stream.

There are many industrial processes where low concentrations of oxygen, below about 1%, must be monitored with great accuracy down to concentrations measured in parts per billion. A typical process might be one in which a hydrocarbon stream is being processed to effect a chemical reaction which is sensitive to the presence of oxygen in the stream in extremely small proportions. In these circumstances, very small quantities of oxygen often constitute serious explosion hazards and it is of extreme importance that oxygen contents be determined with utmost accuracy so that corrective measures may be taken to avert hazardous conditions.

The method and apparatus of this invention depend for operation on the quantitative, i.e., coulometric, reduction of gaseous oxygen with the concurrent liberation of electrons which constitute a flow of current which is a linear function of oxygen concentration in the sample gas. Analyzers of this general type are known in the art, one being described in British Patent 707,323, published April 14, 1954 (corresponding with U.S. Patent 2,805,191, issued September 3, 1957); however, apparatus of this kind hitherto known has been characterized by non-linear response, erratic behavior in use and sensitivity to the ambient environment, so that dependability was seriously impaired.

The objects of this invention are to provide a method and apparatus for the electrolytic analysis of oxygen which is completely quantitative over a wide range of concentration, which is not affected by environment temperature, and which is relatively insensitive to vibration and shock and therefore adapted to operation under adverse plant conditions. Other objects of this invention are to provide an analytical method and apparatus which is selective to oxygen and not interfered with by other gases which may happen to be present, which has a very short time delay in response and which gives an electrical output sufficiently large so that oxygen content can be conveniently read on inexpensive meters or recorded by standard instruments. Still another object is the provision of a method for oxygen analysis which does not necessitate the use of standard samples.

The manner in which these and other objects of this invention are accomplished will become apparent from the detailed description and the following drawings, in which:

Fig. 1 is a longitudinal section of a preferred embodiment of an analytical cell according to this invention.

Fig. 2 is an enlarged sectional view of the electrical connector between the cathode element and the cathode lead.

Fig. 3 is a full sectional view taken on line 3—3 of the connector of Fig. 2.

Fig. 4 is a schematic representation of a complete system for the analysis of oxygen, with provision for check-

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ing operation with a reference gas, gas flow control and pretreatment of the sample before supply to the analytical cell.

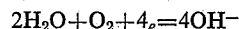
Fig. 5 is a schematic circuit diagram of one type of electrical circuit which can be employed for control of the apparatus of Fig. 4, and

Fig. 6 is a diagrammatic time sequence representation for the reference checking part of the circuit of Fig. 5.

Generally, oxygen analysis according to this invention is accomplished by flowing the gas stream to be analyzed at a predetermined substantially constant rate of flow into a cathodic reduction zone consisting of an aqueous electrolyte solution non-reducible at the analysis potential in contact with a cathode element of surface area sufficient to reduce completely all oxygen contained in the gas stream while maintaining the potential of the cathode element with respect to the electrolyte solution within the range of about -0.10 v. and -1.7 v., and determining the oxygen content in the gas stream as a linear function of the current flow between the cathode element and a reference anode element in contact with the electrolyte solution.

Analysis according to this invention may be conducted on either a continuous or intermittent basis for the determination of oxygen in gas streams; however, by an indirect procedure hereinafter described in detail, it is possible to analyze for oxygen in liquid streams as well as in gas streams.

It is known that, when certain electrode materials are immersed in a body of aqueous electrolyte solution and oxygen is bubbled in contact with one of the pair and with the electrolyte solution, electrolytic reduction of the oxygen ensues, which may be represented by the equation



According to the convention in the art the electrode at which the electrolytic reduction takes place is termed the cathode, whereas the other electrode of the cell is denoted the anode. This convention is observed throughout the following description and it is important to note that the actual potentials existing on the individual electrodes have no bearing on the electrode designations, in the sense that the electrode at which reduction occurs is still referred to as the cathode even though its potential may, in fact, be positive with respect to the associated anode element. Since the anode element is subordinate in function to the cathode element, and also because numerous different materials may be utilized as anodes, it is convenient to refer cathode potentials to that of the solution as reference, and this convention is hereinafter followed.

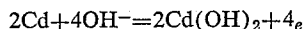
The electrolytic reduction of oxygen occurs within certain limitation regardless of the relative potentials of the cathode and anode elements. A migration of hydroxyl ions from the cathode to the anode will thus occur even where the anode potential is somewhat negative with respect to the cathode, the motivating force being apparently that of diffusion under the competing effect of the law of mass action and the existing cathode potential in the region of the cathode, hereinafter referred to as the "cathodic reduction zone."

It has been found that analytically reliable electrolytic reduction of oxygen occurs within a range of cathode potentials, referred to the electrolyte solution, of between about -0.10 v. and -1.7 v. At potentials more positive than -0.10 v. reduction ceases to be quantitative, while at potentials more negative than -1.7 v. interfering background current results from hydrogen evolution.

Silver and copper reduce oxygen very easily and are preferred cathode materials since, in addition, they are not subject to rapid attack by most suitable electrolyte

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solutions. In contrast, platinum is relatively unsatisfactory as cathode because oxygen reduction takes place at too slow a rate. Electrochemically active metals such as cadmium are preferred as anode materials for the reason that, even if the recharging potential source hereinafter described becomes depleted, the anode will have a reserve capability for continued analytical service. Where cadmium is employed as anode the action occurring at the anode during oxygen analysis may be represented by the following equation:



Thus, if all of the oxygen in the sample gas is reduced according to the equation, oxygen concentration will be a calculable function of the electric current flowing in the circuit connecting the electrodes in accordance with Faraday's law expressing the equivalence of 96,500 coulombs per gram equivalent of oxygen. Cadmium is resistant to corrosion by basic electrolyte solutions, such as KOH, as an example, while lead and platinum are good anode materials for use with both chemically neutral and acidic electrolyte solutions. A wide variety of other materials are suitable for anode service, such as iron for use with basic electrolyte solutions, molybdenum, gold, graphite, stainless steel for use with acidic electrolyte solutions, and tin or antimony for use under neutral conditions. The choice of material for anode fabrication is thus dependent in part on the chemical characteristics of the particular electrolyte solution which is employed and, in addition, the electrolyte solution must be non-reducible within the operating potential range of -0.1 v. to -1.7 v. of the cathode referred to the electrolyte solution.

Electrolytic solutions useful in the practice of this invention include aqueous solutions which are chemically basic, such as 30% KOH or 20% K_2CO_3 , neutral, such as 10% Na_2SO_4 or K_2SO_4 or 20% KHCO_3 , or acidic, such as 5% H_2SO_4 . Alkali metal acetate solutions are also useful, as are many other salt solutions meeting the criteria which have been set forth.

It is essential that all of the oxygen in the sample stream be completely reduced in the cathodic reduction zone, and we have found that very intimate contact of the sample gas with the cathode element and with the electrolyte solution are imperative to dependability of analysis. Sintered metal cathodes having small diameter through-going pores are preferred, however, stacked screens, wire coils or metal shot presenting relatively large surfaces of contact to both gas and electrolyte solution are satisfactory alternatives.

Complete reduction of oxygen is insured where the cathode element dimensions are related to the flow rate of the gas sample therethrough by the following expression:

$$0.7 > \frac{A \cdot D_b}{F \cdot D_e} > 0.002$$

wherein

A is the cross-sectional area of the cathode element in cm^2 ,

D_b is the bulk density (inclusive of voids) of the cathode element in gms./cm^3 ,

D_e is the density of the cathode substance per se in gms./cm^3 , and

F is the flow rate of the gas stream in $\text{cm}^3/\text{min.}$ at standard conditions (i.e., 25°C. and 760 mm. Hg absolute pressure).

A gas sample flow within the range of about 10 cm^3 to about $250 \text{ cm}^3/\text{min.}$ is desirable in oxygen analysis according to this invention, the lower limit being set by difficulties encountered in measuring accurately low gas flows, and also because at lower flow rates leaks of air into the system result in proportionately greater errors in determination. The upper limit is determined by convenience in flow measurement and also by excessive pres-

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sure drop accompanying a high sample flow rate. In practice, the sample flow rate is, of course, held substantially constant so that the reduction current is the more readily related to the oxygen content of the sample.

In a typical instance wherein a porous silver cathode 1.0 cm^2 in cross-section (A) was employed, the bulk density (D_b) was 5.25 and the density of the cathode substance per se (D_e) was 10.5. A flow rate of $100 \text{ cm}^3/\text{min.}$, referred to standard conditions of 25°C. and 760 mm. Hg absolute pressure, (F) on substitution in the relationship expression gave the following:

$$\frac{1.0 \times 5.25}{100 \times 10.5} = 0.005$$

which is greater than 0.002 and, therefore, the combination meets the requirements.

It is, of course, essential to operation that, with zero oxygen content supplied to the cathodic reduction zone, zero signal current be generated in the electrical circuit including the analyzing electrodes. Minor amounts of reducible impurities contained in the electrolyte solution, gradual corrosive action of the electrolyte solution on the analytical cell housing, inherent surface potentials of the electrodes in contact with the electrolyte solution, and a slight tendency for some anode material to deposit on the cathode element and thus give a concentration cell effect result, in the aggregate, in a small background current which may be as high as about $20 \mu \text{ amp.}$ This background current is thus so small that usually it is negligible when analyzing for oxygen in concentrations above about 25 p.p.m. When the analysis of lower concentrations of oxygen is required it is preferred to apply a counter biasing D.-C. potential across the electrodes of the order of 20–50 mv. which maintains the anode at a slightly negative potential with respect to the cathode. Thus, with a Cd anode-Ag cathode analytical cell, the Cd anode might be maintained at -0.8 v. potential while the Ag cathode might be at -0.75 v. potential, both referred to the electrolyte solution.

The effects obtained with the biasing potential are multiple. The most important is probably that there is electrolytic suppression of anode material migration to the cathode, thus eliminating the concentration cell effect. Almost equally important is the fact that the cathode is largely reserved for oxygen reduction, and thus remains highly stable over long periods in this service, any impurities in the electrolyte being mainly reduced at the anode where there is essentially no effect on the accuracy of analysis. Under these circumstances zero current flow can be made to correspond to zero oxygen content with a surprising constancy.

As hereinbefore indicated with respect to the anode of the analytical cell, the chemical reaction occurring at the anode tends to oxidize the material, such as Cd, which, in effect, changes the composition of the anode electrode with the passage of time unless corrective measures are taken. This effect is comparable to what occurs during service in a secondary battery, and the technique of recharging can be employed advantageously to restore the anode surface to its original purity. Recharging can be effected by applying a suitable D.-C. potential in a sense making the anode cathodic for a period sufficient to reduce the surface oxide to elemental metal and can be done periodically, which requires that the analyzer be taken out of service. It is preferred, however, to provide a second electrolytic circuit across which is applied a suitable low recharging potential of the order of about 1.5 v. between the anode and an electroconductive mass other than the cathode, but in contact with the electrolyte solution, of such nature that the anode is maintained cathodic with respect to the mass. If the analytical cell housing is fabricated from an electroconductive nonreadily attackable material the recharging voltage can be conveniently applied across the anode element as cathode with respect to the

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housing as anode. The recharging potential thereby continuously reduces any oxide deposits on the anode thus making possible continuous analysis service and, at the same time, conferring additional stability to operation. The application of the recharging potential does not, of course, affect the potential maintained across the analytical electrodes because a separate circuit through the electrolyte solution exists as regards these elements.

Where a noble metal such as platinum is utilized as the anode, the level of the electrode potential with respect to the electrolyte solution might be inadequate for analysis. A supplementary potential applied between the platinum anode and the cell housing in the same manner as described for the recharging voltage affords a remedy for this condition, however, the term "recharging" is a misnomer as applied to the function, because platinum does not oxidize on the surface objectionably as occurs with cadmium.

Referring to Fig. 1, a preferred embodiment of analytical cell according to this invention comprises the cylindrical housing 5, which may comprise a length of 1" nominal size stainless steel pipe about 16" long, closed at the bottom with a welded cap and provided with a flange 6 formed at the top of the tube for attachment with cell cap 7 by bolts 8. Two tapped holes are provided radially inwardly of bolts 8 for attachment of adapters 11 and 12, which frictionally secure in place gas sample supply tube 13 and gas sample exit tube 14, respectively.

Supply tube 13 is sealed against gas leakage at the top by a polymeric plug 18, which is provided with a longitudinal hole through which is passed electrical conductor 19 in gas-tight contact with the plug. The gas sample is introduced through port 20, opening into the top of tube 13, connected at the outer end to the gas supply line 65 (refer Fig. 4) of the apparatus, and leaves the cell through exit port 50 connected to line 69 hereinafter described. The interior of tube 13 is open for the free flow of sample therethrough, except for the small space occupied by the thin wire extension of conductor 19 which is passed out of contact with tube 13 from the top to the bottom, where it is joined to metal connector 24 as shown in Fig. 2. Connector 24 is a tubular sleeve which is drilled axially from the top over about 60% of its length with an enlarged bore 25 for passage of the gas sample stream therethrough. The lower part of connector 24 is drilled to a somewhat smaller diameter 26 to receive in tight frictional engagement bridging conductor 27 (refer Fig. 1) terminating in cathode element 28.

As shown in Fig. 3, the lower end of connector 24 is slotted diametrically at 90° intervals around the periphery with through-going slots 31 through which the gas sample has free passage. Connector 24 and the lower end of the extension conductor 19 are electrically insulated from tube 13 by encasement in a tubular polymeric sleeve 32, which is friction-fitted within the lower end of tube 13.

Tube 13 is provided at the lower end with an electrode mount 36 fabricated from an electrical insulator such as polyvinylchloride or the like. Mount 36 is provided with a bored recess 37 within the upper end of which is mounted cathode element 28, which is retained in position by a shrink fit peripherally and by hot pressing down upper lips 38 of the mount. A radial passage 39 is provided in mount 36 for supply of the gas sample to the underside of porous cathode element 28. The cross length of bridging conductor 27 is electrically insulated where it lies outside of mount 36 and passage 39 facilitates the insertion of the jaws of small pliers for pressing the left-hand uninsulated end of 27 into the body of cathode element 28, to thereby establish good electrical contact therewith. As a final step, recess

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37 is sealed off with a liquid-tight plug of casting resin 40.

The anode element of the cell consists of cadmium electrode 45 which is of the cadmium impregnated pencil type supported by a sintered nickel matrix. An anode $\frac{1}{4}$ " in diameter and 3" long has proved satisfactory in service. The electrical circuit for the cell is completed through insulated electrical conductor 46 attached to the top of electrode 45, which connection is strengthened by a polyethylene sleeve 47 interiorly filled with potting resin 48. A polymeric plug 49 corresponding to plug 18 seals adapter 12 against gas leakage around conductor 46.

The cathode element 28 hereinabove described is particularly intended for use with an alkaline electrolyte which, for the specific apparatus described, is a 25% KOH solution, which is preferably carried to about the level indicated at A of Fig. 1, although this level is not critical so long as a substantial length of anode 45 is immersed. Cathode element 28 may be in the form of a porous sintered silver plug of about $\frac{1}{2}$ " diameter and $\frac{3}{4}$ " long provided with through-going gas passage pores of a diameter of several microns size. The same design of silver cathode may be employed in conjunction with a 10% KHCO₃ electrolyte solution and a lead anode for the analysis of oxygen in carbon dioxide, the carbon dioxide remaining unaffected by the electrolyte solution, in which case the caustic scrubbing sample pretreatment hereinafter described is omitted.

As hereinbefore brought out, oxygen concentration is indicated by this invention in terms of an electric current linearly related to oxygen concentration, 1 p.p.m. by volume of oxygen in the original sample producing an electrolytic current of 26.4 μ a./100 cc./min. of gas sample flow measured at 25° C. and atmospheric pressure. Indication is provided by a microammeter or other current measuring instrument 52 connected in series with the electrodes as indicated in Fig. 4. For accuracy and stability of measurement, particularly at low oxygen concentrations, the imposition of a counter biasing E.M.F. to the electrodes is essential as hereinafter described. Also, in a continuous type analytical instrument it is preferred to utilize a somewhat more complex system of sample processing and instrument operation checking, and one such system is detailed as to sample processing and electrical circuitry in Figs. 4 and 5, respectively.

Referring to Fig. 4, sample gas is supplied to the apparatus through gas supply line 53 which is connected to the normally open port of 3-way solenoid valve 54, the outlet of which is connected to gas line 55. The normally closed port of valve 54 is connected to gas line 56, which constitutes the outlet of oxygen remover 57 hereinafter described. Where the CO₂ in the sample stream is less than about 1% and the accuracy of analysis is such that the slight error resulting from measurement of the rate of gas flow after CO₂ has been removed can be tolerated, it is desirable to remove the CO₂ by caustic scrubbing prior to delivery of the sample to the analytical cell indicated generally at 4. This is the case because otherwise there is a tendency for carbonate precipitation to occur, with resultant clogging of the pores of the cathode. If the CO₂ content is higher than about 1%, or if accuracy requirements are more severe, substitution of a neutral electrolyte as hereinbefore described for the basic electrolyte is preferred. Even with substitution of electrolyte, however, it is desirable to prescrub the sample, as by passage through a bath of the same composition as the electrolyte solution employed, in order to humidify the sample and prevent clogging by dehydration within the porous cathode.

Assuming CO₂ is to be removed, sample is introduced into scrubber 64 through line 55 which discharges into a diffuser 62, which may be a sintered metal wafer or

the like, which is immersed in a liquid absorbent for CO₂, such as KOH solution. CO₂-free gas leaves the scrubber through line 65 in open connection with the port 20 of analytical cell 4. The flow of gas sample through the analytical cell is controlled by conventional regulator 70, which may be a commercial diaphragm-type pressure regulating valve adapted to maintain the downstream pressure at a set point in the range of about 0-10 lbs./sq. in. gage, in series with adjustable restrictor 71, which may be a needle valve or like flow restrictor, connected in gas exit line 69. Sample gas leaves restrictor 71 through line 72 connected to the inlet of rotameter 73, which discharges to the atmosphere through a vent 74.

Since the analyzer of this invention functions in accordance with Faraday's Law, no calibration of the instrument is necessary, nevertheless, an overall check on operation can be obtained by the use of a coulometric oxygen generator and a reference gas supply in the following manner. The oxygen generator 78 is preferably of the electrolytic type, such as that disclosed in application S.N. 505,597 of Frederick A. Keidel. Since the apparatus of this invention functions on small concentrations of oxygen, a supply of diluting gas for the oxygen output of generator 78 must be provided. This reference gas may be commercial nitrogen containing only about 20 p.p.m. of oxygen, which oxygen is removed by scrubbing in an alkaline 5% KOH solution, 79, having 0.05% added sodium beta anthraquinone sulfonate contained in oxygen removal scrubber 57. Solution 79 is maintained in chemically reduced, and hence oxygen-absorbing, state by means of amalgamated zinc metal rods (not shown) immersed therein. A trap 80 is connected in series with reference gas line 81 to collect any liquid backflow from scrubber 57 and the reference gas is supplied to solution 79 through a diffuser 82, which may be a sintered metal wafer or a similar distributor.

The complete electrical circuit for the apparatus is shown in Fig. 5. If a unitary case (not shown) is utilized to house the entire instrument, an electrical ground 88 is provided in connection therewith and, also, with analytical cell housing 5. Power is supplied from a conventional 60 c. A.-C. source through conductors 89 and 90, which are preferably connected through two terminals of a terminal strip 91. Although A.-C. operated solenoid valves can be utilized, we prefer to provide a D.-C. supply for operation of the solenoid valve 54 of Fig. 4, the operating coil 92 of which is shown schematically in Fig. 5. The D.-C. supply network, indicated generally at 93, is a conventional R-C half wave rectifier utilizing, however, a silicon rectifier 96 which is connected through terminal strip 91 via electrical conductor 97 and switch S₄ to hot A.-C. line 89 and through lead 98 with coil 92. Normally open switch S₄ is connected in circuit with conductor 97 to permit periodic operation of the rectifier in response to motor timer 100 hereinafter described.

Motor timer 100 may be a 4-cam 30 minute-cycle, conventional time switch of a type such as commonly employed in domestic washing machines and dishwashers for the cycle control thereof, with cams cut in conformity with the time cycle depicted in Fig. 6, which is connected in circuit across A.-C. supply line 89 and neutral line 90 through conductor 101, which is provided with manual switch S₂ and manual starter switch S₁, and conductor 102. Pilot light 106 is shunt-connected around motor timer 100 through normally closed switch S₅ operated by the timer. Timer 100 also operates switch S₃ which is normally connected to ground 107, but which has a shunt contact 108 in the coulometric generating circuit, which is connected to oxygen generator 78 through leads 109 and 110.

The coulometric generating circuit comprises the network connected across terminal strip 91, including 90 v.

B battery 112 which is in series with tapped resistor 113 (typically of one megohm resistance) and resistor 114 (typically of 100 K ohms). On the other side of switch S₃ there is connected a microammeter 115, preferably in the range 0-500 μ amp., when concentrations of reference oxygen of up to about 20 p.p.m. are involved, and of higher range for greater concentrations. The circuit with lead 109 is preferably completed through silicon diode 116 which isolates meter 115 from reverse current flow when switch S₃ is opened, thereby restoring the meter to zero position when the coulometric generator circuit is inactive. The negative side of battery 112 is connected through terminal strip 91 to electrical ground at 117.

The remainder of the circuit has three separate functions, namely, the connection of the analytical cell with a recorder, the imposition of a counter biasing E.M.F. on the electrodes of cell 4 to confer stability of operation, and electrical recharging of the cadmium anode 45. These functions are conveniently accomplished through a common network to which the analytical cell is connected through leads 46 and 19 (refer also Fig. 1). The cell electrode circuit is completed through resistor 122 (typically 10 ohms) and tapped resistor 123, a conventional recorder (not shown) being connected to this circuit through leads 124 and 125.

A counter biasing E.M.F. of about 50 mv. is imposed on cathode element 28 to maintain it positive with respect to anode 45 when no oxygen is present in the sample stream as hereinbefore described. This E.M.F. is supplied by source 129 which may be a 1.5 v. battery, such as a conventional flashlight type. The biasing circuit is completed through terminal strip 91 by resistor 130 (typically 250 ohms) which serves to proportion the biasing E.M.F. applied across resistor 122, which is preferably of the order of 20 to 50 mv., the circuit containing resistors 122 and 130 functioning as a voltage divider in the network completed through lead 131 with source 129.

Since the cadmium electrode 45 tends to be oxidized to Cd(OH)₂ during operation of cell 4, it is desirable to recharge the electrode, which can be done continuously without interference with operation as an analyzer by use of the network hereinafter described. This network comprises resistor 132 connected at one end to the positive side of source 129 and grounded at the other end. The negative side of source 129 is in circuit with lead 46 through lead 131 as hereinbefore described. Consequently, electrode 45 is effectively the cathode of a cell of which the anode is the inside wall of housing 5, the cell electrolyte completing the circuit. Since the cell is grounded, as hereinbefore mentioned, the electrical circuit back to source 129 is complete. A value of resistor 132 of about 180 ohms has proved especially effective for low concentrations of oxygen, whereas a value of about 60 ohms is better where high concentrations of oxygen are analyzed for, because higher charging currents are thereby obtained to counteract the higher rate of oxidation encountered.

The operation of the analyzer of this invention, apart from the timer circuit and the auxiliary circuits responsive to the timer circuit, is as follows. As shown in Fig. 4, the sample gas is introduced to the apparatus through line 53 and solenoid valve 54 which, in the absence of timer operation, maintains open communication with the line 55 leading to CO₂ removal scrubber, or humidifier, 64. The sample gas may be an elemental gas such as, but not limited to, hydrogen, nitrogen, ethane, ethylene, or other gases, or mixtures of any of the foregoing one with another, which contain up to about 20% of oxygen and down to as low as about 0.1 part per million or less.

The flow rate of gas sample may be as high as about 250 cm.³/min. with full quantitative removal of oxygen with a sintered silver cathode of the dimensions de-

scribed, but flow rates of the order of 200 cm.³/min. are preferred. In cell 4 the oxygen is reduced to the hydroxyl ion form and these ions, on migration to anode 45, generate a driving voltage for the cell of about 0.9 v. To insure quantitative reduction of the oxygen, a cathode 28 of large surface area is essential and, contrary to the teachings of the prior art, intimate mixture of the gas stream with the electrolyte and contact with the electrode should be effected by violent agitation of the electrolyte in the vicinity of the cathode element by bubbling the sample gas therethrough. The cathode construction hereinabove described in detail is so effective in reducing oxygen that past electrode history, temperature, pressure, sample composition, and the like, have no interfering effect on conduct of the analysis.

It will be understood that the electrodes of cell 4 are connected practically in short circuit, since resistor 122 is very small, and the voltage drop thereacross at very low current flows of the order maintained during operation is very small. Under these circumstances, background current constitutes interference which reduces analytical efficiency. The imposition of the counter biasing E.M.F. of about 50 mv. from source 129 effectively raises the voltage level of operation to the point where background current is so reduced that there is no effect on the signal representative of oxygen content and the analyzer is possessed of marked stability.

As previously described, during operation cadmium hydroxide forms on anode 45 which, if allowed to accumulate, would eventually alter the inter-electrode potential difference and introduce inaccuracy into the analysis. This difficulty is circumvented by continuous recharging from source 129 which imposes, through lead 131, a negative potential on anode 45, so that element 45 in effect becomes cathodic with respect to housing 5 of cell 4. Accordingly, Cd(OH)₂ is reduced at electrode 45 at approximately the same rate as it is formed, the oxygen ions migrating to the inside wall of housing 5, which is grounded, thus completing the electrical circuit of the recharging network through resistor 132 as hereinbefore described. Molecular oxygen bubbles form on the inside wall of housing 5 and, under quiescent conditions, would constitute an interference to analysis; however, the rapid flow of sample gas past cathode element 28 gives a sparging action to the gas which sweeps the oxygen away from the housing out of cell 4 through sample gas exit line 69.

The analyzer of this invention is extremely sensitive to oxygen and has a very rapid response time to the oxygen content of a flowing sample of the order of about 10 seconds. The apparatus is also of very high sensitivity, which results in the development of an appreciable electrical signal representative of oxygen content, and has a very high stability and freedom from drift and from aging effects.

Operation of the analyzer of this invention entails merely passing the gaseous sample through the apparatus as hereinbefore described, observing the generated current reading and relating this reading to the sample flow rate per unit time.

In a typical test run an analyzer constructed in all respects as hereinbefore described was supplied with a mock sample consisting of 260 cc./min. flow of nitrogen referred to standard conditions (i.e. 25° C. and 760 mm. Hg absolute pressure). This nitrogen was the highest quality, oxygen-free nitrogen commercially available; however, even after passage through oxygen-removing scrubber 79 (Fig. 4) it was found that residual oxygen remained therein in the amount of 0.3 p.p.m. which generated a steady analyzer current of 20μ amperes. Consequently, it was necessary to correct subsequent instrument readings by this amount.

To check operation of the analyzer, oxygen generator 78 (Fig. 4) was operated first at an arbitrarily selected constant current level which gave a steady reading of 120μ amperes for a period of approximately 10½ hrs.

The volume attributable to the generated oxygen in this and other runs was so small as to be imperceptible to the apparatus flow meter and was accordingly ignored in the appraisal calculations. Allowing for the residual oxygen correction equivalent to the 20μ amperes hereinbefore mentioned, the analyzer indication was found to be exactly equal to the measured current input to generator 78, thus verifying absolutely quantitative operation on the part of the analyzer. This was followed by another test in which generator 78 was operated at a current level corresponding to a theoretical analyzer indication of 500μ amperes for a period of approximately 20½ hrs. The analyzer indication during this test was a very steady 520μ amperes, again showing complete conformance to the known oxygen input when correction was made for the residual oxygen contamination of the nitrogen supplied.

While the foregoing describes the determination of oxygen in a gas stream, it will be understood that the oxygen content of liquids can be readily determined by first transferring the oxygen from the liquid to a gas stream which is subsequently processed in the same manner as hereinabove described for gas containing oxygen initially. The oxygen can be stripped from a liquid sample by flowing the liquid through a packed column in opposition to a stream of oxygen-free carrier gas, such as nitrogen, for example. A column ¼" inside diameter and 12" long packed with glass beads has proved effective in the removal of oxygen from a liquid sample. In a typical test, it was found that one p.p.m. by weight of oxygen in the original liquid sample resulted in an electrolytic current of 60μ amp./cm.³/min. of liquid sample. Since sample flow rates of 10 cc./min. are practical and, since recorder sensitivities of several microamperes full-scale are readily obtainable, a full-scale response corresponding to 10 parts/billion of oxygen in a liquid sample is obtainable with the apparatus.

The analyzer hereinabove described is completely operable without any additional equipment; however, motor timer 100 and the auxiliaries connected in circuit therewith are useful for periodic checks of the condition of the apparatus, and would disclose any anomalies in operation which might not be otherwise apparent. It will be understood that the coulometric generator is, in fact, an operating condition checking device, rather than a standardizing auxiliary, since the analyzer operates according to Faraday's Law and no standardization is, therefore, necessary.

Referring to Figs. 5 and 6, a malfunctioning test on the analyzer can be initiated by the operator at will by closure of switch S₁, whereupon motor timer 100 initiates a test cycle, which requires a time interval of about 30 minutes during which the analyzer is taken out of sample analysis service. In practice, a malfunctioning test might be made once every two weeks, or even less frequently, during periods suited to manufacturing convenience, as during shutdowns for repairs of manufacturing equipment.

Switch S₂ of Fig. 5 is normally in closed position but can be opened manually by the operator if it is desired to stop motor timer 100 at any point in its cycle. With switch S₂ closed, a timer cycle is initiated by depressing spring-biased switch S₁ to closed position for an interval sufficient to start rotation of the cam which actuates switches S₅, S₄ and S₃. This is indicated by pilot light 106, which is illuminated at all times except during operation of motor timer 100, and which goes out when switch S₅ is closed on contact 135. A mere momentary depression of switch S₁ is all that is required to initiate the timing cycle, as indicated by the S₅ bar of the timing diagram of Fig. 6. Approximately 10 seconds after start of the timing cycle, switch S₄ is closed by the timer as indicated by the broken line representation of Fig. 5 so that switch S₄ closes on contact 136, thereby activating the half-wave rectifier containing recti-

fier element 96, thus imposing D.-C. power on solenoid valve coil 92 of valve 54, Fig. 4. Valve 54 thereupon closes connection between sample line 53 and flow line 55 and establishes, instead, communication between line 56 and line 55. Assuming that reference gas under pressure is available in line 81, the reference gas is stripped of oxygen by passage through oxygen remover 57, from which it passes valve 54 and flows to CO₂ removal scrubber 64. The oxygen-free reference gas then passes through line 65 and through analytical cell 4 for a period of approximately 15 minutes, which is amply sufficient to permit checking of the zero of the apparatus under stabilized conditions. At the 15 minute point of the cycle, as indicated in Fig. 6, coulometric generator switch S₃ is closed on contact 108 by motor timer 100, as indicated by the broken line representation of Fig. 5. The coulometric generator thereafter produces a known quality of oxygen electrolytically, which is added to the test gas in about the proportion equivalent to half of full scale analyzer sensitivity, so that analytical cell 4 receives a known concentration of oxygen for the interval remaining in the timing cycle. Equilibrium is very rapidly obtained within the analytical cell, and the remainder of the approximately 15 minutes during which the coulometric generator functions is ample to permit checking the analyzer and its circuitry for any inaccuracies which might come to light as a result of the checking cycle. If additional time is required for corrective adjustments or repairs to the circuit or the fluid flow lines, the operator can open switch S₂ and immobilize motor timer 100 for the balance of its cycle until it is convenient to permit further run-out.

From the foregoing it will be understood that we have provided a method and apparatus for oxygen analysis of exceptional dependability, selectivity and sensitivity, and that this invention may be altered in many ways within the scope of the art without departure from the essential spirit of the invention, wherefor it is intended to be limited only within the scope of the following claims.

What is claimed is:

1. An apparatus for the coulometric analysis of oxygen in a flowing gas stream consisting in combination of an electrolytic cell provided with a porous cathode element selected from the group consisting of silver and copper and an anode element in contact with an aqueous electrolyte solution non-reducible at the analysis potential, said anode element being substantially inert chemically with respect to said electrolyte solution, means maintaining said cathode element at a potential of between about -0.1 v. and -1.7 v. with respect to said 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 complete electrolytic reduction of the oxygen in said flowing gas stream, means imposing a D.-C. electrical bias between said cathode and anode elements in opposition to the voltage generated by said electrolytic cell and in an amount reducing electrical background interference existing in said cell during said analysis, and means for determining the content of oxygen in said flowing gas stream as a function of the elec-

tric current flow between said cathode element and said anode element.

2. An apparatus for the coulometric analysis of oxygen in a flowing gas stream consisting in combination of an electrolytic cell having an electrically conductive housing and provided with a porous cathode element selected from the group consisting of silver and copper and an anode element in contact with an aqueous electrolyte solution non-reducible at the analysis potential, said anode element being substantially inert chemically with respect to said electrolyte solution, means maintaining said cathode element at a potential of between about -0.10 v. and -1.7 v. with respect to said 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 complete electrolytic reduction of the oxygen in said flowing gas stream, means imposing a D.-C. electrical bias between said cathode and anode elements in opposition to the voltage generated by said electrolytic cell and in an amount reducing electrical background interference existing in said cell during said analysis, means for imposing a D.-C. electrical recharging potential between said anode element as cathode and said housing as anode, and means for determining the content of oxygen in said flowing gas stream as a function of the electric current flow between said cathode element and said anode element.

3. An apparatus for the electrolytic analysis of oxygen in a flowing gas stream according to claim 2 wherein said D.-C. electrical bias between said cathode and anode elements in opposition to the voltage generated by said cell is between about 20 mv. and about 50 mv., and wherein said D.-C. electrical recharging potential is between about 0.8 v. and about 1.7 v.

4. An apparatus for the electrolytic analysis of oxygen in a flowing gas sample according to claim 2 provided with means for temporarily removing said apparatus from analytical service and means for supplying to said electrolytic cell a gas stream containing a known concentration of oxygen to thereby check the operation of said apparatus for malfunctioning.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,898,282

August 4, 1959

William M. Flook, Jr., et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 11, line 17, for "quality" read -- quantity --.

Signed and sealed this 29th day of December 1959.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents