Feb. 11, 1969 A. R. MYERS ET AL 3,427,238

ELECTROLYTIC TITRATION APPARATUS

Filed Nov. 18, 1964 Sheet 1 of 3

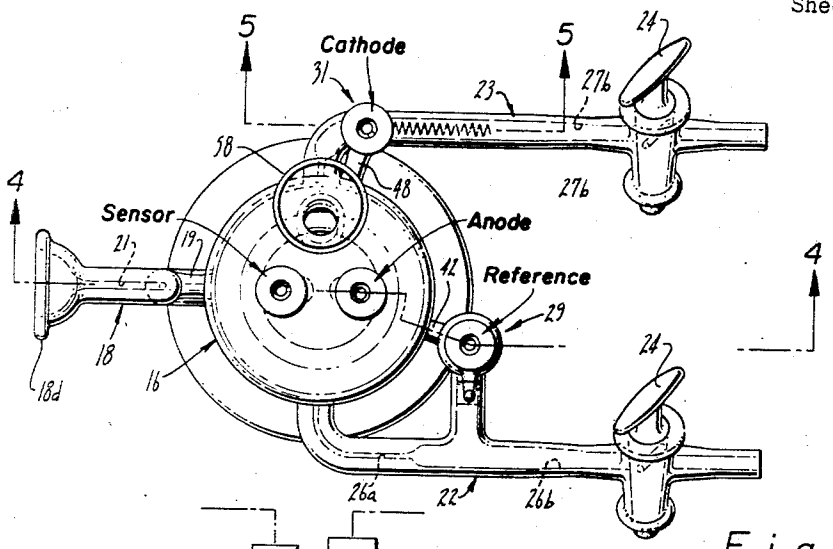


Fig. 2

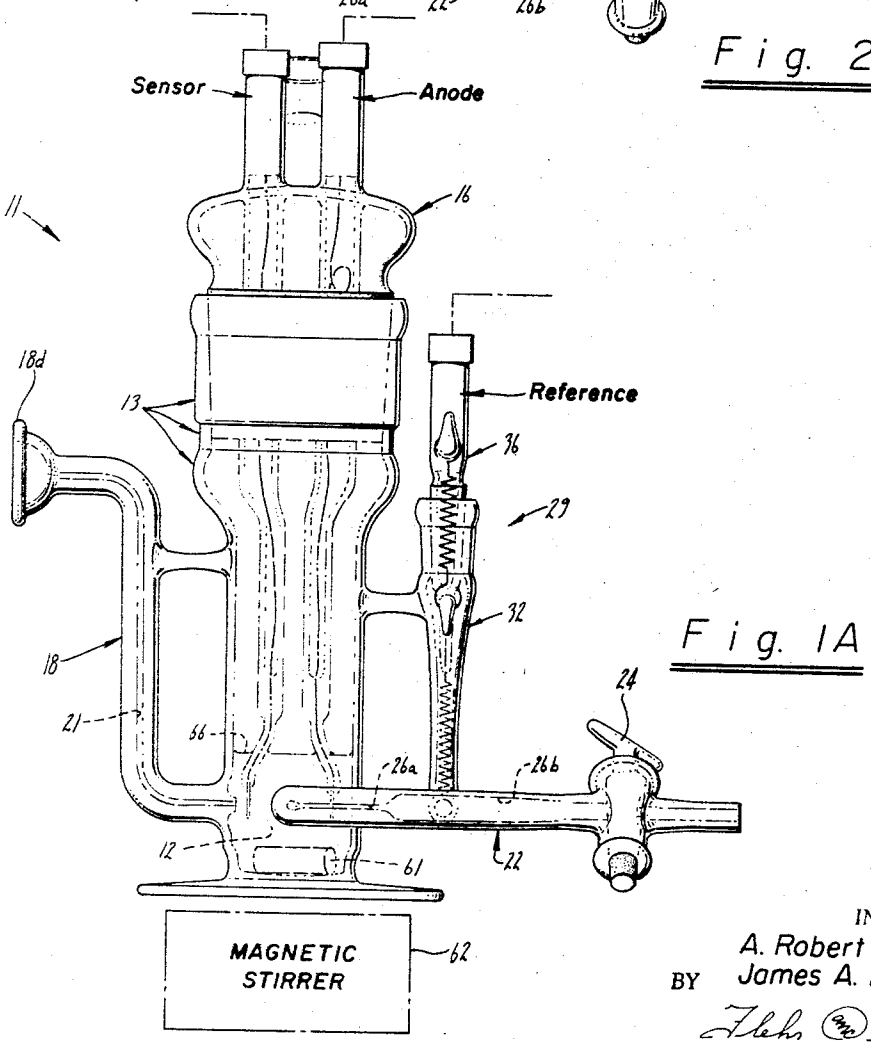


Fig. 1A

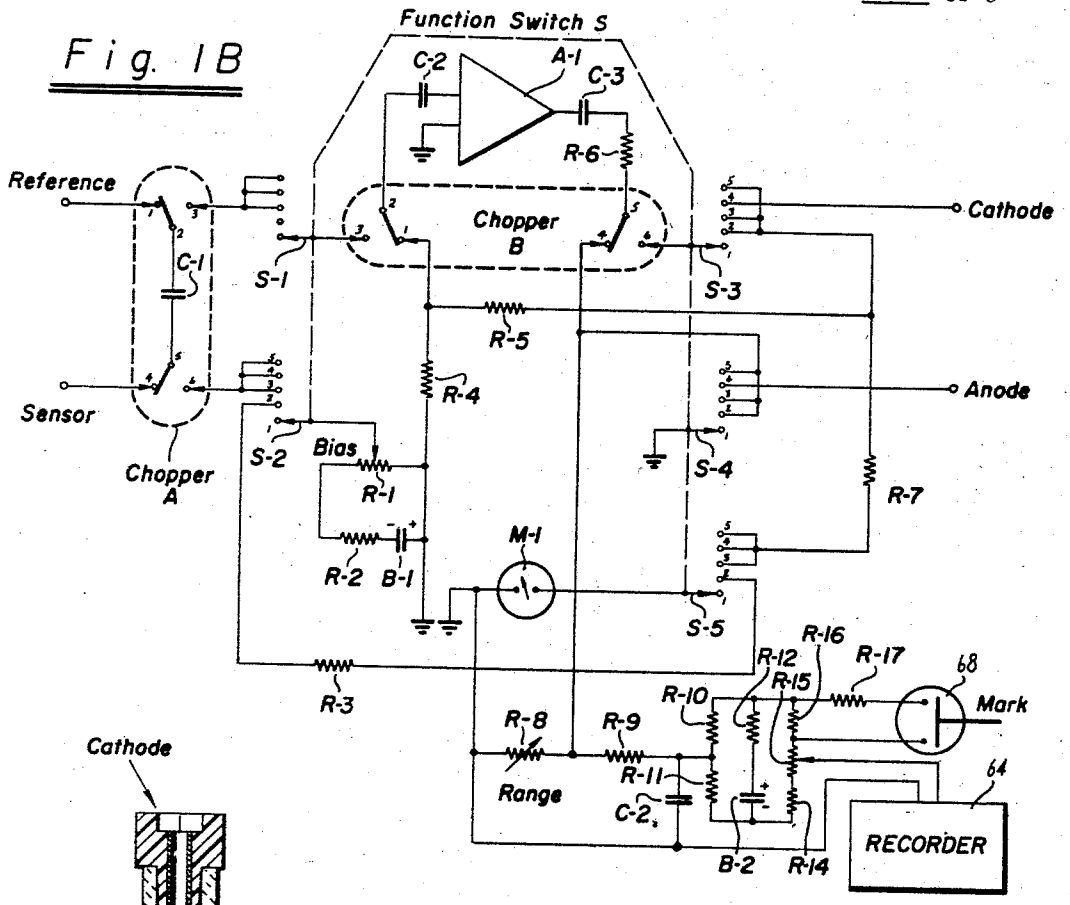
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ELECTROLYTIC TITRATION APPARATUS

Filed Nov. 18, 1964 Sheet 2 of 3

Fig. 1B



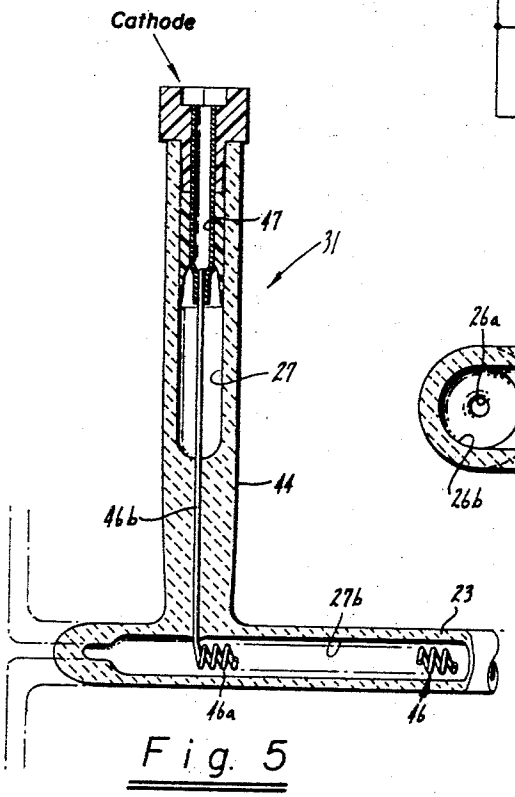


Fig. 5

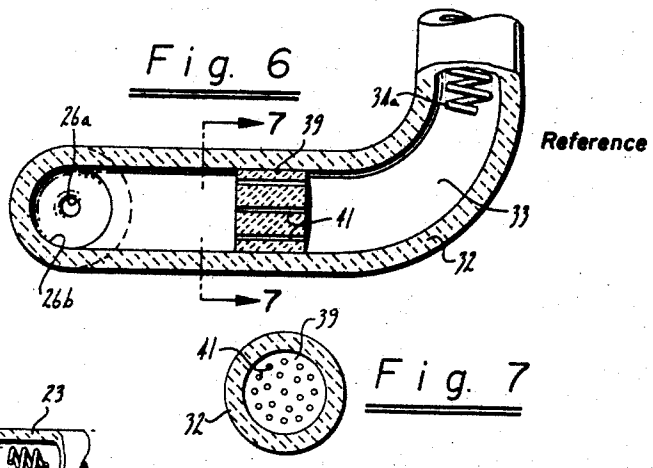


Fig. 6

Fig. 7

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ELECTROLYTIC TITRATION APPARATUS

Filed Nov. 18, 1964 Sheet 3 of 3

Fig. 3

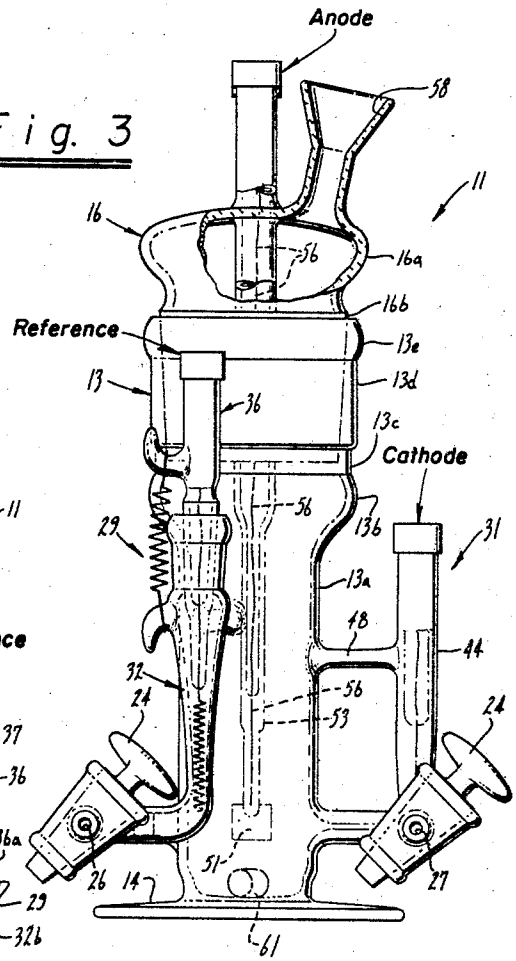
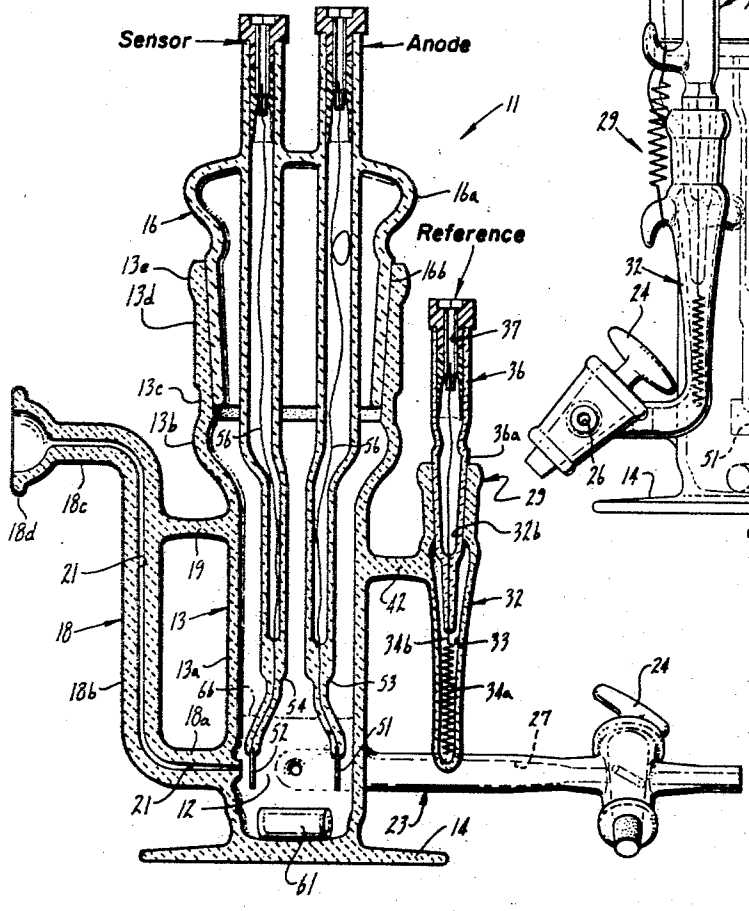


Fig. 4



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ELECTROLYTIC TITRATION APPARATUS

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Int. Cl. B01k 3/00

ABSTRACT OF THE DISCLOSURE

Electrolytic titration apparatus which has chopper means for supplying power to the generating electrodes only when the sensing electrode assembly is disconnected and which has isolation means for providing a predetermined impedance between the sensing electrode and the reference electrode of the sensing assembly.

This invention relates to an electrolytic titration apparatus and more particularly to an electrolytic titration apparatus which can be utilized for macro, micro, and sub-micro analysis.

In U.S. Patent No. 3,032,493, there is disclosed electrolytic titration apparatus which can be utilized for micro-analysis. Although such electrolytic titration apparatus has been found to be commercially successful, there is still a need for apparatus with increased sensitivity and particularly an improved signal to noise ratio.

In general, it is an object of the present invention to provide an electrolytic titration apparatus which has increased sensitivity.

Another object of the invention is to provide apparatus of the above character in which an improved titration cell is utilized.

Another object of the invention is to provide apparatus of the above character in which the signal to noise ratio is substantially improved.

Another object of the invention is to provide apparatus of the above character in which improved circuitry havin novel isolation features is provided.

Additional features and objects of the invention will appear from the following description in which the preferred embodiment is set forth in conjunction with the accompanying drawings.

Referring to the drawings:

FIGURES 1A and 1B show an electrolytic titration apparatus incorporating the present invention in which FIGURE 1A is a top plan view of the titration cell and FIGURE 1B is a circuit diagram of the circuitry connected to the titration cell.

FIGURE 2 is a top elevational view of the titration cell.

FIGURE 3 is a front elevational view of the titration cell shown in FIGURE 2.

FIGURE 4 is a cross-sectional view taken along the line 4—4 of FIGURE 2.

FIGURE 5 is an enlarged cross-sectional view of the cathode assembly of the titration cell.

FIGURE 6 is an enlarged cross-sectional view of the reference assembly of the titration cell.

FIGURE 7 is a cross-sectional view taken along the line 7—7 of FIGURE 6.

The titration cell **11** shown in the drawings and forming a part of the electrolytic titration apparatus includes means containing an electrolyte and defining a reaction zone **12** for carrying out the titration process as hereinafter described. This means is shown in the form of a substantially cylindrical vessel or cell **13** formed of a suitable material such as glass. As can be seen, the vessel **13** is provided with a straight-sided cylindrical portion **13***a* which is formed integral with a footing **14** that serves to support the cylindrical portion **13***a* in a substantially vertical position. The vessel **13** is also provided with an enlarged or flared portion **13***b*, a cylindrical recessed portion **13***c*, a straight-sided portion **13***d* and an enlarged upper portion **13***e*.

A cap **16** is mounted in the top portion of the vessel **13** and serves to enclose the top of the vessel. The cap is provided with a dome-shaped upper portion **16***a* and a relatively straight-sided portion **16***b*. The cap **16** is formed of a suitable material such as glass and the outer surface of the portion **16***b* is provided with a surface which can mate with the inner surface of the portion **13***d* of the vessel **13**. Thus, the inner surface of the portion **13***d* and the outer surfaces of the portion **16***b* are ground so that both surfaces mate with each other to provide a relatively tight fit in which the portion **13***d* serves as the female portion and the portion **16***b* serves as the male portion of a ground glass joint which is formed between the cap **16** and the vessel **13**.

The titration cell is formed with a gas inlet tube **18** which serves as means for introducing the constituent to be titrated or analyzed into the titration cell. As can be seen from FIGURE 2, this inlet tube **18** is connected to the lower portion of the vessel **13** and is provided with a portion **18***a* which extends outwardly therefrom. A portion **18***b* extends upwardly to a position which is substantially above the level of the electrolyte within the cell. The tube is provided with another portion **18***c* which extends in a horizontal outward direction. The tube **18** is also provided with an enlarged funnel-shaped portion **18***d*. An integral brace **19** is provided for connecting the upper portion of the tube **18** to the vessel **13** to give additional support to the tube **18**. A small passage **21** having a diameter of .013 of an inch is formed in the inlet tube **18** and extends from the funnel portion **18***d* into the reaction zone **12** in the vessel **13** as can be seen from FIGURE 2.

A pair of drain tubes or side arms **22** and **23** are also mounted on the lower portion of the vessel **13** and extend outwardly therefrom in a horizontal direction. A stop cock **24** is provided in each of the drain tubes **22** and **23**. Passages **26** and **27** are provided in the drain tubes **22** and **23**, respectively, and extend through the length thereof and open into the reaction zone **12** formed within the vessel **13**. As can be seen from FIGURES 1A and 2 of the drawings, the passages **26** and **27** have varying cross-sectional areas with the passage having a relatively small dimension as it enters the reaction zone and having a relatively large cross-sectional area at an intermediate portion of the drain tubes.

A reference electrode assembly **29** is connected to the drain tube **22** and a cathode assembly **31** is connected to the drain tube **23**. The reference electrode assembly consists of a vertical arm **32** which is connected to the side arm **22**. The arm **32** is provided with a vertically extending passage **33** which connects with the enlarged portion **26***b* of the passage **26** in the side arm **22** so that a liquid bridge is formed between the arm **32** and the reaction zone **12** within the vessel **13**. A reference electrode **34** of a suitable metal, as hereinafter described, is removably disposed within the passage **33**. The electrode **34** is supported by support member **36**. The support member **36** is provided with a ground glass surface **36***a* which mates with a female ground glass portion **32***b* formed in the upper part of the vertical arm **32** to form a ground glass joint. The reference electrode **34** is provided with a coil portion **34***a* and a straight portion **34***b* which is mounted within the lower portion of the support member **36** and which is connected to a female connector **37** disposed

within the upper portion of the support member 36. As can be seen particularly from FIGURE 2, the support member 36 mates with the vertical arm 32 and the reference electrode 34 is mounted in the support member 36 in such a manner that the lower extremity of the reference electrode extends from the bottom of the passage 33.

Means is provided for establishing consistency of the liquid bridge which is formed in the passage 33 and consists of a cylindrical member 39 which is disposed within the lower extremity of the passage 33 below the reference electrode 34. This member 39 is provided with a large number of uniform diameter, small capillary passages 41 which connect the passage 33 with the passage 26 to provide a uniform impedance. An integral brace 42 connects the upper portion of the vertical arm 32 to the vessel 13 to give additional rigidity to the arm 32.

The cathode electrode assembly 31 consists of a vertical arm 44 which is connected to the side arm 23. A generating cathode 46 is mounted in the portion 27*b* of the passage 27 and is provided with a coil or helical portion 46*a* and a straight portion 46*b* which extends upwardly into the arm 44 and is sealed with respect thereto. The portion 46*b* is connected to a female receptacle 47 mounted in the arm 44. As can be seen, the generating cathode 46 is disposed in a horizontal position within the passage 27. An integral brace 48 is provided for connecting the upper part of the arm 44 to the vessel 13 to provide adidtional support for the arm 44.

A generating anode 51 and a sensor or sensing element 52 are disposed within the vessel 13 within the reaction zone 12. Both the generating anode 51 and the sensing element 52 are in the form of flat rectangular plates and are formed of suitable materials as hereinafter described. Means is provided for supporting the generating anode 51 and the sensing element 52 within the reaction vessel and consists of substantially parallel glass tubes 53 and 54 which are secured to the top 16 in such a manner so that they extend downwardly from the top in a substantially vertical direction. The generating anode 51 and the sensing element 52 are connected by leads 56 to female sockets provided in the upper extremities of the tube similar to that hereinbefore described in connection with the reference electrode and the generating cathode. The cathode 46 and the anode 51 serve as generating electrodes whereas the reference electrode 34 and the sensing electrode 52 serve as a sensing electrode assembly.

A funnel 58 is provided in the top cap 16 to facilitate introduction of eletcrolyte into the reaction zone 12 within the vessel 13.

In examining the arrangement of the electrodes, it can be seen that the sensing element 52 is positioned in front of the opening 21 provided in the gas inlet 18 and that the generating anode 51 is removed 180° therefrom. The inlets to the side arms 22 and 23 are also spaced 180° apart and are removed 90° from the inlet opening 21.

Means is provided for stirring the electrolyte within the reaction chamber 12 and consists of a metal cylinder 61 which is rotated within the reaction zone 12 by suitable means such as a magnetic stirrer 62.

The titration cell 11 with its magnetic stirrer 62 are connected to circuitry shown in FIQURE 1B to provide a complete electrolytic titration apparatus. As shown in FIGURE 1B, this circuitry is connected to a recorder 64 of a suitable type such as a strip chart recorder. The circuitry includes a number of elements including chopper A and chopper B which are pointed out during the description of operation of the apparatus.

Operation of the electrolytic titration apparatus may now be briefly described as follows. Let it be assumed that the vessel 11 has been filled with electrolyte through the funnel 58 to a suitable level such as the level 66 as shown in FIGURE 4. Electrolyte is then permitted to pass into the side arms 22 and 23 by opening the stop cocks 24.

Now let it be assumed that the fluid stream containing the sample to be titrated is passed through the passage 21 of the inlet tube 18 through the capillary opening and into the electrolyte within the reaction zone 12. In the case of a gas stream, excess inert gas similar to the sample carrier may be added to the main stream to ensure rapid and complete introduction of the sample into the cell. This higher rate of flow reduces the possibility of the electrolyte or the solution in the reaction chamber from backing up into the inlet tube 18. Also, in this same manner, sample hold-up on the wetted surface of the inlet tube 18 is substantially reduced, if not prevented.

During the time that the sample is introduced, the magnetic stirrer 62 is placed in operation to cause stirring of the electrolyte and to cause the sample to be mixed rapidly and uniformly distributed through the electrolyte.

As the sample enters the reaction zone 12, it goes into the solution within the vessel 13 to produce a change in the potential between the sensing electrode 52 and the reference electrode 34. The manner in which the sample goes into the solution need not be known. It may be by reaction or hydration, or a combination of both. It makes no difference as far as the present analysis is concerned.

As can be seen, the circuitry includes principally two choppers, chopper A and chopper B, and power means in the form of an amplifier A–1. Both the choppers and the amplifier are conventional. The choppers are, however, of the 60 cycle synchronous type. A function switch S is also provided which has five different wipers S1, S2, S3, S4 and S5 engaging five levels of contacts, with each level of contacts being numbered 1 through 5. The first position for the function switch is when the wiper arms are on the #1 contact. In this position, the apparatus is in an "off" condition. The second contact of each bank can be identified as the "bias read" position of the function switch S. In this position, the bias supplied to the wiper S2 is adjusted by adjusting the potentiometer R1. This bias is obtained from the battery B1 through the fixed resistor R2. In the #2 position of the function switch, a bias voltage is supplied through a resistor R3, through the wiper S5 and through the meter M1. By watching the meter M1, the desired amount of bias as, for example, 250 millivolts, can be readily obtained. As is well known to those skilled in the art of operating titration cells, this bias level is a function of the silver ion concentration in the electrolyte.

After this is completed, the function switch is shifted to the #3 position, which can be called the "generator read" position, to actually determine the potential of the electrolyte within the reaction zone by connecting the output of the amplifier A to the meter M1. This makes it possible to check whether or not a fresh electrolyte or additional electrolyte is required to bring the electrolyte up to the desired potential.

After it has been established that the bias potential and the potential of the electrolyte are substantially identical as, for example, 250 millivolts, the function switch S4 is shifted to the fourth position, which may be called the "operate" position. This will automatically bring the titration cell to the bias potential which is supplied to the wiper S2.

Now let it be assumed that the fluid stream containing the sample to be titrated is passed through the inlet tube 18, through the capillary passage 21 into the electrolyte in the reaction zone 12. As the sample enters the reaction zone 11, it goes into the solution to produce a change in potential. This change in potential is caused by a decrease in the silver ion concentration which demands current flow between the generating cathode and anode. This current flow in the reaction zone 12 is such that it causes an incerase in silver ion concentration. This current flows for a period of time and is recorded on the recorder 64 in a manner hereinafter described.

The choppers A and B operate synchronously, that is, when contacts 1 and 2, and 4 and 5 of chopper A are closed, the corresponding contacts of chopper B will also

be closed. The choppers A and B operate at a 60 cycle rate.

When the chopper A and chopper B are in the positions shown in FIGURE 1B, that is, with contacts **1** and **2**, and **4** and **5** of each of the choppers closed, the potential being sensed by the sensor electrode is being measured by the capacitor C1 connected across the contacts **2** and **5** of chopper A. At the same time the input and output of the amplifier A1 are grounded through R4 and R8, respectively. Under this condition, it can be seen that the reference sensor electrodes are completely isolated from the generating anode and cathode because there is no direct connection between the sensor and reference electrodes and the generating anode and cathode.

When the choppers A and B are operated so that contacts **2** and **3**, and **5** and **6** of each of the choppers are closed, the potential which was sensed by the sensor electrode and placed on the capacitor C1 is compared with the bias voltage supplied by the wiper S2. Any difference between the bias voltage and the voltage on the capacitor C1 is supplied through the coupling capacitor C2 to the amplifier A–1 through closed contacts **2** and **3** of chopper B. In view of the fact that choppers A and B operate synchronously, the signal being repeatedly applied to the capacitor C2 is pulsating DC which is coupled to the AC amplifier A–1 which amplifies the same and supplies the same to the capacitor C3 and resistor R6 through the closed contacts **5** and **6** to place a potential on the cathode-anode circuit in the form of a pulsating DC. Current flows between the cathode and the anode to cause the generation of titrant. The amount of current which flows is stored by the capacitor C3. As is well known to those skilled in the art, the amount of reactant generated is directly proportional to the current generated. The charge on the capacitor C3 is supplied to the recorder when the contacts **4** and **5** of the chopper B are closed through the resistor R9 and through the resistive bridge network consisting of the resistors R10, R11, R14 and R15. Generation of the titrant continues until sufficient titrant has been generated to cause the system to reach a null condition, at which time the potential sensed by the sensing electrode is substantially identical to the bias electrodes so that a signal is no longer supplied to the amplifier A–1 and no potential is supplied to the cathode.

If an excess of titrating agent is generated in error, the polarity of the signal at the indicating or sensing electrode is reversed to cause current to flow in the opposite direction from the output of the amplifier and to reverse the normal electrolytic action until the excess of the titrating agent has been removed.

The output of the amplifier A–1 in positions **2**, **3** and **5** of the function switch S is supplied directly to the meter M1 so that the meter indicates the amplitude of the output voltage developed by the amplifier. The resistor R7 is a calibration resistor for the meter M1 when it is reading the output voltage of the amplifier. The resistor R8 is a range resistor and establishes a range of currents which are recorded by the recorder **64**. The resistor R4 protects the contacts of the chopper B. Resistor R5 serves as a load resistor for the amplifier on the generator read and standby positions of the function switch S.

The potentiometer R1 provides an adjustment for the bias voltage. The resistor R2 establishes a full scale voltage across the resistor R1, and the resistor R3 is provided for calibrating the meter M1.

The resistor R9 and the capacitor C2 provide an integrating or filter network which reduces the amplitude of small noise voltages being developed in the circuitry. The resistors R10, R11, R14, R15 and R16 form a bridge circuit in which a battery B1 of a suitable voltage such as 1.45 volts in series with the resistor R12 establishes a predetermined voltage across the bridge. The resistor R15 serves as a center control for the recorder. A resistor R17 in series with a marking switch makes it possible for the marking switch to unbalance the bridge to generate an upswing on the recorder pen to mark a point on the recorder.

It should be pointed out that for substances titratable with silver ion, the sensor and generator anode are silver, and the generator cathode is platinum, and the reference is silver in saturated silver acetate. The supporting electrolyte is 70–85% acetic acid. For those substances titratable with iodine, the electrodes are of noble metal and the reference electrode is platinum in saturated triiodide, the supporting electrolyte is 0.04 to 0.05% KI and 0.4% acetic acid. Other electrodes and electrolyte systems can be used. However, the iodine and silver titrations are the most common.

The titration cell is particularly sensitive because the sensor electrode is placed directly adjacent the gas inlet so that a much larger signal output is provided for a given quantity of sample injected into the electrolyte. Another factor is the fact that the generating anode **51** is positioned 180° from a gas inlet so, therefore, for that reason it is exposed to less turbulence caused by the bubbles formed upon introduction of the sample into the electrolyte. This is because any bubbles which are formed normally dissipate about the time liquid circulates around the anode **51**. Greater sensitivity is also obtained because the reference electrode arm **22** and the cathode arm **23** enter the reaction zone of the cell 180° apart. It can be seen that the arrangement of the electrodes is such that the electrodes are positioned vertically so that the same strata of liquid is scanned by the electrodes. Thus, the anode is disposed at substantially the same vertical elevation as is the sensor.

The plug or member **39** which is provided with small passages **41** is particularly important in that it ensures uniformity of impedance in the liquid path formed between the passage **33** and the passage portion **26***a* of the passage **26**.

One particularly important feature of the present apparatus is that there is no interaction between the reference and sensor electrodes and the anode and cathode generating electrodes because of the use of the synchronous choppers. This feature makes it possible to place the electrodes in any position in the cell and also makes it possible to place the sensor directly over the gas inlet thereby making it possible to obtain a larger signal for a given sample introduced into the cell.

From the foregoing, it can be seen that with the electrolytic titration apparatus herein disclosed, an error signal is amplified, polarized and coupled to the generating electrode circuit by another chopper. There is no servo system and, therefore, there is no dead band. The circuitry provides a very tight control and extremely fast response. In the off position, the reference and sensor electrodes are completely removed from the circuit by center off chopper swingers. In the standby position, the generating electrodes are disconnected from the circuit to permit scrubbing a sample stream. The amplifier output can then be switched into the cell when desired to complete the titration. The sensor electrode is isolated from the effects of the applied generator voltage by the phasing of the chopper contacts. A greatly improved signal to noise ratio is also obtained.

We claim:

1. In an electrolytic titration apparatus, an electrolytic cell comprising means containing an electrolyte forming a reaction zone, means for introducing a fluid containing the constituent to be titrated into the electrolyte, generating electrodes disposed in the electrolyte, a sensing electrode assembly disposed in the electrolyte, and circuit means connecting said generating electrodes and said sensing electrode assembly and causing the generating electrodes to generate a titrant in accordance with the amount of constituent introduced into the electrolyte, said circuit means including storage means, power means having an input and an output and chopper-operated means for connecting the storage means alternately to the sensing

electrode assembly and to the input of the power means, and connecting the generating electrodes to the output of the power means in such a manner that power is supplied to the generating electrodes from the power means only when the sensing electrode assembly is disconnected from said storage means to thereby isolate said sensing electrode assembly from said generating electrodes, and the electric fields thereabout.

2. An apparatus as in claim 1 together with indicating means and wherein said chopper-operated means connects the output of the powers means alternately to the generating electrodes and to the indicating means.

3. An apparatus as in claim 1 wherein said chopper-operated means includes a pair of synchronous choppers each having two sets of contacts.

4. An apparatus as in claim 1 wherein said sensing electrode assembly includes a reference electrode and a sensing electrode together with means for isolating the reference electrode from the reaction zone, said means for isolating including a member having a plurality of relatively small capillary passages of a predetermined number extending therethrough of substantially uniform diameter, said member serving to provide a predetermined impedance between the reference electrode and the electrolyte in the reaction zone.

5. An apparatus as in claim 1 wherein said generating electrodes consist of a cathode and an anode and said sensing electrode assembly consists of a sensing electrode and a reference electrode, wherein said circuit means includes a bias supply and indicating means and wherein said chopper-operated means includes first and second choppers, each of said choppers having first and second sets of contacts, each set of contacts comprising a common contact and first and second switch contacts, means connecting said storage means between the common contacts of said first and second sets of contacts of said first chopper, said first switch contact and said first set of contacts of said first chopper being connected to said reference electrode and said first switch contact of said second set of contacts of said first chopper being connected to the sensing electrode, means for connecting the second switch contact of the first set of contacts of said first chopper to the second switch contact of said first set of contacts of said second chopper, means connecting the second switch contact of said second set of contacts of said first chopper to the bias supply, means connecting the common contact of said first set of contacts of said second chopper to the input of the power means, means connecting the common contact of the second set of contacts of said second chopper to the output of the power means, means connecting the first switch contact of the first set of contacts of the second chopper to ground, means connecting the first switch contact of the second set of contacts of the second chopper to the indicating means and means connecting the second switch contact of the second set of contacts of the second chopper to the cathode electrode of the generating electrodes.

6. Apparatus as in claim 5 wherein said power means is an amplifier and wherein said means connecting the common contact of said first set of contacts of the second chopper to the input of the power means includes a capacitor connected to the input of the amplifier and wherein said means connecting the common contact of the second set of contacts of the second chopper to the output of the power means includes a capacitor connected to the output of the amplifier.

7. Apparatus as in claim 5 wherein said first and second choppers are synchronously driven.

8. In an electrolytic titration apparatus, an electrolytic cell comprising means containing electrolyte forming a reaction zone, means for introducing a fluid containing the constituent to be titrated into the electrolyte, a pair of generating electrodes disposed in the electrolyte, a sensing electrode and a reference electrode disposed in the electrolyte, and means for isolating the reference electrode from the reaction zone, said means including a member having a plurality of relatively small capillary passages of a predetermined number extending therethrough of substantially uniform diameter, said member serving to provide a predetermined impedance between the reference electrode and the electrolyte in the reaction zone.

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U.S. Cl. X.R.

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