April 26, 1966 M. L. ROBINSON 3,248,309

AUTOMATIC TITRATION APPARATUS AND METHOD

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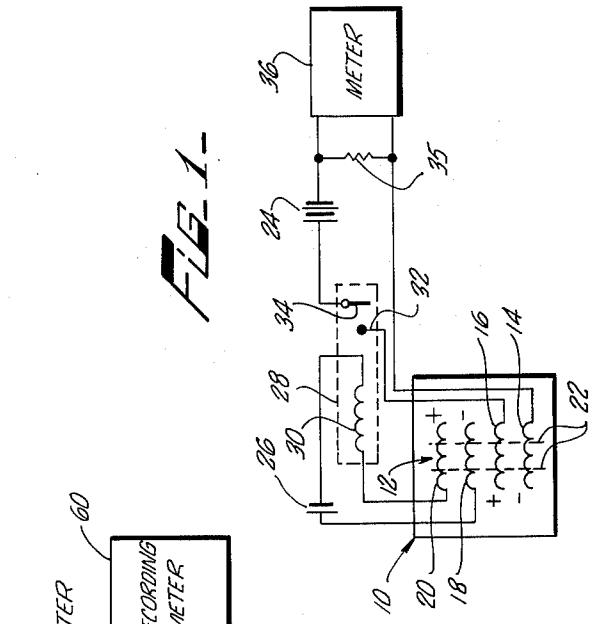

FIG. 1

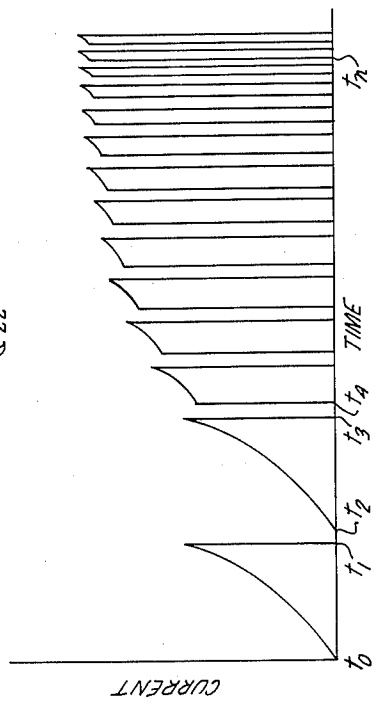

FIG. 3

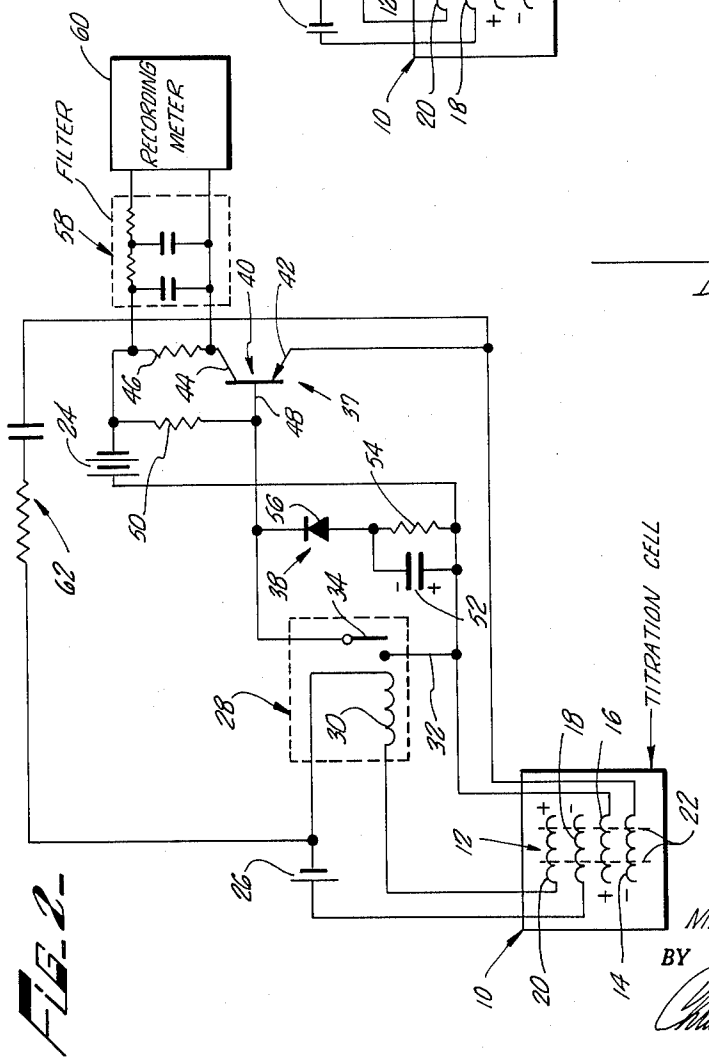

FIG. 2

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AUTOMATIC TITRATION APPARATUS AND METHOD

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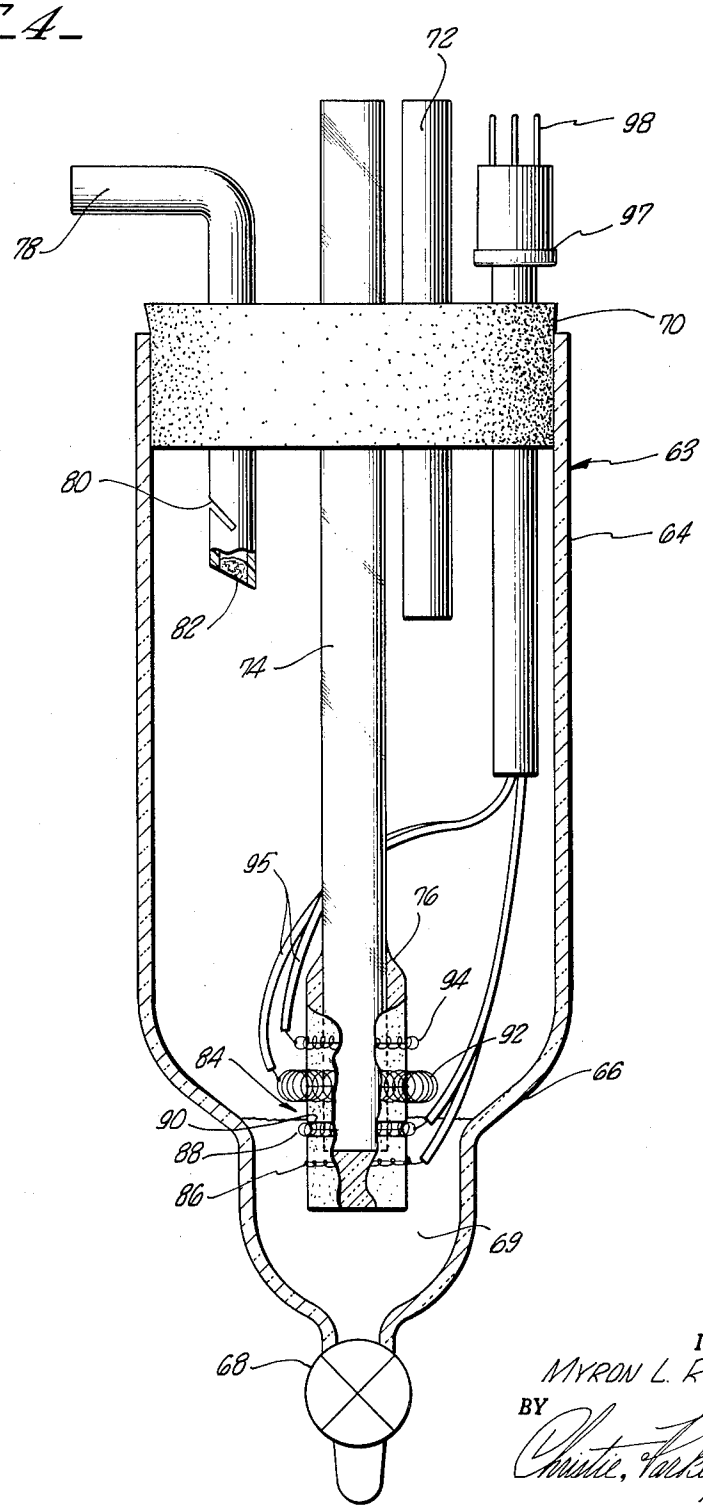
FIG. 4



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AUTOMATIC TITRATION APPARATUS AND METHOD

Filed Sept. 11, 1961 3 Sheets-Sheet 3

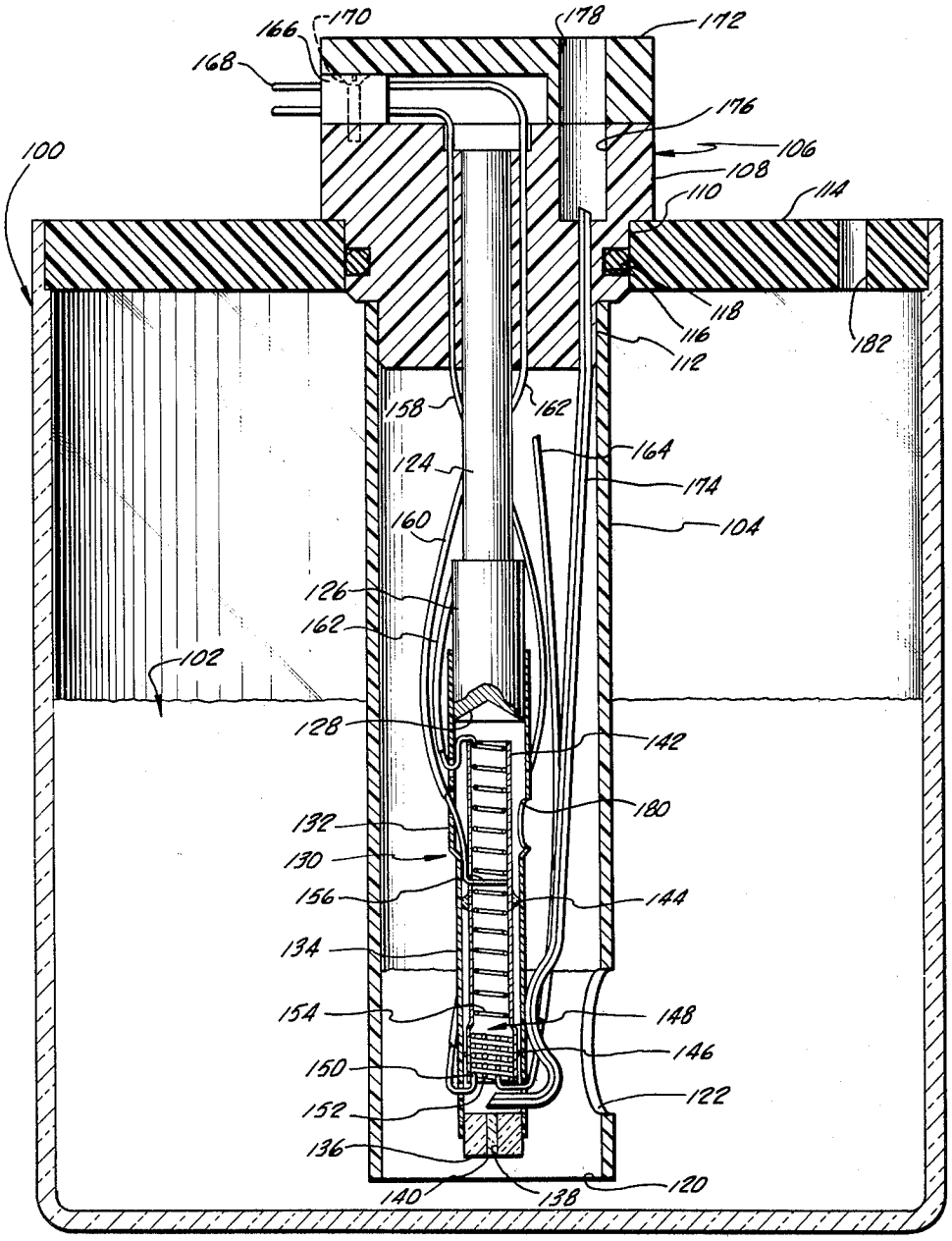

FIG. 5

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AUTOMATIC TITRATION APPARATUS AND METHOD

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17 Claims. (Cl. 204—1)

This invention is directed to improvements in automatic titration apparatus and, more particularly, to an improved titration apparatus employing novel titration cell designs which provide for substantially continuous titration.

Titration systems for automatically determining the concentration of a reactive agent present in a fluid by electrolytic generation of reagents are well known. Generally, such titration apparatus utilize relative complex combinations of electrical circuitry and titration cell design to obtain a measure of concentration of the reactive agent in a fluid which is being sampled. The titration cells generally have separated compartments which house isolated electrode units with separate filtering and cleaning arrangements.

Such cells require an appreciable amount of electrolytic solution for operation and are therefore relatively bulky and are not readily transportable in their assembled form. Due in part to the volume of electrolytic solution required by such cell designs, the cells do not respond rapidly to rapid changes in concentration of the reactive agent. In addition to lacking rapid response time to rapid changes in concentration of the reactive agent such cell designs require an appreciable time to stabilize after the addition of new solution or following a period of inoperation. Further, such cell designs generally do not provide means for continuously monitoring the concentration of a reactive agent present in a fluid and are relatively insensitive to concentrations of less than one part per million.

Due to the above, such titration apparatus have proved unsatisfactory for processes requiring continuously operating means for detecting rapid changes in the concentration of a reactive agent over wide ranges of concentration. One example of a process requiring such a type titrating apparatus is in the handling of high propellant fuels where it is mandatory for human health to be able to continuously detect the presence of and rapid changes in concentration of dangerous noxious vapors in ranges from one tenth part per million to at least 500 parts per million.

In view of the above, the present invention provides an automatic, continuous titration apparatus which responds rapidly to changes in the concentration of a reactive agent over a range extending from one tenth part per million to at least 500 parts per million.

In accomplishing this the present invention employs a simplified control circuit in combination with a novel titration cell design which is extremely compact and rugged and requires less than two milliliters of electrolytic solution for proper operation.

Briefly, the present invention in a basic form includes a titration cell having a small quantity of electrolytic solution containing ions of a titrating agent and means for continuously bubbling a fluid containing a reactive agent along a predetermined fluid path through the solution. Positioned in the fluid path is a compact electrode assembly comprising first and second generator electrodes spaced

along the fluid path and first and second sensor electrodes spaced along the fluid path and separated from the generator electrodes. Coupled to the generator electrodes are means for developing a current signal to generate the titrating agent from the ions at one of the generator electrodes. Coupled to the sensor electrodes are means for generating a current signal between the sensor electrodes which is a function of the concentration of the titrating agent in solution. The means for developing a current signal between the generator electrodes is responsive to the current signal between the sensor electrodes such that the titrating agent is only generated by the generator electrodes when the current signal between the sensor electrodes falls to a predetermined reference value. The generator electrode current flow is metered to provide a measure of reactive agent concentration in the fluid.

In operation, when the fluid containing an unknown amount of the reactive agent is bubbled into the solution along the fluid path, the reactive agent fully combines with the titrating agent in the region of the generator electrodes. This reduces the concentration of the titrating agent in the solution. The reduction in the concentration of the titrating agent in solution is sensed by the sensor electrodes and results in a reduction in the current flow therebetween to the predetermined reference value. A current is then developed between the generator electrodes to generate the titrating agent at the generator electrodes and increase the concentration of the titrating agent in solution. With the increase on concentration of the titrating agent in solution, the current flow between the sensor electrodes again increases with a corresponding cessation of current flow between the generator electrodes. In this manner, since the current flows between the generator electrodes only when it is necessary to compensate for a reduction in concentration of the titrating agent due to the presence of the reactive agent, the current flow between the generator electrodes may be utilized to provide a measure of the concentration of the reactive agent in the fluid.

Thus, the present invention by continuously bubbling the fluid containing unknown amounts of a reactive agent through the electrolytic solution and detecting a current flow which is a function of the concentration of the reactive agent present in the fluid provides an automatic, continuous titration apparatus. Due to the close alignment of the generating and sensor electrodes, the titration cell of the apparatus has a rugged, compact design and requires only a small amount of electrolytic solution for operation. The use of a small amount of electrolytic solution results in a reduction in the time required for the generator electrodes to generate an amount of titrating agent sufficient to compensate for changes in concentration of the reactive agent being bubbled into the electrolytic solution. In this manner, the present invention operates rapidly to detect changes in concentration in the reactive agent and is ideally suited for use in processes where the rapid continuous detection over a wide range of concentrations of dangerous noxious vapors is required.

For a more complete understanding of the automatic, continuous titrating apparatus of the present invention as well as a detailed understanding of the structural arrangement of the novel titration cell designs of the present invention, reference should be made to the following detailed description which is to be considered with the drawings, in which:

FIGURE 1 is a schematic representation of a basic form of the titration apparatus of the present invention;

FIGURE 2 is a schematic representation of a preferred form of the automatic titration apparatus of the present invention;

FIGURE 3 is a graphical representation of the current output from the titration system represented in FIGURE 2;

FIGURE 4 is a sectional view of one embodiment of the titration cell in accordance with the present invention; and

FIGURE 5 is a sectional view of another embodiment of the titration cell of the present invention which is particularly adapted to use in the detection of fuel vapors.

Referring specifically to the drawings, FIGURE 1 is a schematic representation of a basic form of the automatic, continuous titration apparatus of the present invention. As represented, the titration system includes a titration cell represented generally at **10**. Preferred embodiments of the titration cell **10**, which may be employed in the titration apparatus, are described in detail in connection with FIGURES 4 and 5. Accordingly, for an analysis of the overall titration apparatus of the present invention, only the generic features of the titration cells are here discussed.

As will be described in detail in connection with FIGURES 4 and 5, the titration cell includes an electrolytic solution containing ions of a titrating agent. The titrating agent is a substance or element which combines in a known proportion with a reactive agent in a fluid which is introduced into the solution containing the titrating agent. By knowing the amount or concentration of either the reactive agent or the titrating agent required to reach a predetermined state of balance in the solution the amount or concentration of the titrating agent or reactive agent respectively may be determined. In the automatic titrating apparatus of the present invention the determination of such concentration is arrived at automatically by a coulometric system of electrically generated reagents within a titration cell and an amperometric system coupled to the cell for detecting the predetermined state of balance in the solution at which state the current for electrically generating the reagent is a measure of concentration.

By way of example only, bromine may be utilized as the titrating agent in the titration cell **10**—the known or determinable rate of generation of bromine in solution providing a means for determining the concentration of a reactive agent in a fluid which is passed through the solution.

In brief, to determine the concentration of the reactive agent, such as by-products of sulphur or fuel vapor containing hydrazine, the ions of the titrating agent in solution (bromide ions) are electrolyzed to generate a predetermined concentration of the titrating agent in solution. The predetermined concentration of the titrating agent is arrived at by sensing means which senses the concentration of the titrating agent to produce a sensor current which in turn regulates the generation of the titrating agent. Thus, in response to additions of a reactive agent to the solution which combine with and hence reduce the concentration of the titrating agent below the predetermined level, means responsive to the sensor current are energized for generating the titrating agent to compensate for the reduction in concentration. By monitoring the operation of the means for generating the titrating agent the concentration of the reactive agent may then be determined.

To provide such means for determining the concentration of a reactive agent in a fluid which is monitored by passing samples through the aqueous electrolytic solution, the titration cell **10**, as represented, includes an electrode assembly **12** for generating the titrating agent from solution and sensing the concentration of the titrating agent to provide means for determining the concentration of the reactive agent. The electrode assembly has a first

generator electrode **14**, a second generator electrode **16**, a first sensor electrode **18**, and a second sensor electrode **20**. The generator and sensor electrodes are spaced from each other along a common path denoted by the broken line **22** which diagrammatically represents the path of flow of the fluid which is introduced into the cell. The fluid which is introduced into the cell bubbles through the solution to combine with the titrating agent and pass upward through the generator electrodes and sensor electrodes in succession.

The generator electrodes **14** and **16** are coupled in series to a direct current source represented by the battery **24**. The battery **24** preferably develops a voltage of three (3) or more volts and when connected to the generator electrodes causes a current to flow between the generator electrodes thereby causing the titrating agent (bromine) to be generated by electrolytic oxidation at the generator electrode **16**.

A source of potential represented by the battery **26** is coupled in series with the sensor electrodes **18** and **20** such that the sensor electrode **18** is maintained at a negative potential relative to the sensor electrode **20**. The battery develops a voltage between the sensor electrodes and is preferably maintained in a range of 0.25 to 0.5 volt. In this manner a potential difference is maintained between the sensor electrodes which is just below a threshold voltage required to generate hydrogen therebetween. Accordingly, a polarizing film of hydrogen forms on the sensor electrode **18** to inhibit current flow between the sensor electrodes. However, the polarizing film of hydrogen which is formed on the sensor electrode **18** is readily depolarized by the presence of the titrating agent bromine in the region of the sensor electrode **18**.

Thus, bromine generated at the generator electrode **16** and bubbled upward into the region of the sensor electrode causes a depolarization of the thin film of hydrogen on the sensor electrode **18**. The bromine is electrolytically reduced at the sensor electrode **18** while the bromide ions are electrolytically oxidized to form bromine at the sensor electrode **20**. Thus in operation, the sensor electrodes do not affect the concentration of the titrating agent (bromine) in solution.

Due to the electrolytic oxidation and reduction a current flows in the sensor circuit which is a function of the concentration of bromine in solution. As will be described hereafter the sensor current varies from a predetermined magnitude corresponding to a predetermined concentration of bromine with variations in concentration of bromine in solution. Thus, as a fluid containing a reactive agent is bubbled along the fluid path **22** into the region of the electrode assembly **12**, the reactive agent combines with the bromine generated by the generator electrodes to reduce the concentration of bromine in solution. The reduction in concentration of bromine is sensed by the sensor electrodes to produce a reduction in the sensor current. The sensor current and reduction thereof is utilized in a manner hereinafter described to provide means for controlling current flow between the generator electrodes such that the generator current flow provides a direct measure of the concentration of the reactive agent present in the fluid.

To provide means for such control of the current flow between the generator electrodes, the titrating apparatus of the present invention basically includes means **28** in series with the battery **24**, which is sensitive to current flow in the sensor circuit to connect and disconnect the battery **24** from the generator electrodes. By way of example, the means **28** may include a switching means such as a current sensitive relay which operates to open the series path between the battery **24** and the generator electrodes **14** and **16** when a predetermined magnitude of current is flowing in the sensor circuit and close the series generator path when the magnitude of the sensor current is decreased in response to a reduction in the concentration of the titrating agent. Thus, the switching

means operates to connect the batte y in series with the generator electrodes to provide a generation of bromine in solution to counteract the reduction in concentration of the titrating agent due to the presence of the reactive agent in the fluid being bubbled in the solution. When the concentration of the titrating agent in solution is again sufficient to cause the predetermined magnitude of current to flow in the sensor circuit, the switching means operates to disconnect the battery from the generator electrodes. In this manner the switching means functions as a rapid acting on-off device to produce an intermittent current flow between the generator electrodes which provides a measure of the concentration of the reactive agent present in the fluid.

As illustrated, by way of example, in FIGURE 1 the switching means includes a current sensitive relay represented at 28. The relay 28 has a coil 30 connected in series between the battery 26 and the sensor electrode 20 such that the sensor current passes therethrough. The relay 28 also includes a fixed contact member 32 which is coupled to the generator electrode 16 and a movable contact member 34 for contacting the contact 32. The relay 28 is a normally open relay and closes in response to a current passing through the coil 30 by causing the movable contact member 34 to impinge the fixed contact member 32. The relay 28 functions to connect and disconnect the battery 24 from the generator electrodes 14 and 16. Thus, when a current flows in the sensor circuit, the relay 28 is closed to disconnect the battery 24 from the generator electrodes while in the absence of current flow in the sensor circuit the relay 28 is open, thereby connecting the battery 24 to the generator electrodes to provide means for generating bromine in the titration cell 10. Accordingly, the relay 28 functions to halt the generation of the titrating agent at a concentration for which sufficient sensor current flows to operate the relay. In this manner the predetermined concentration of the titrating agent and the corresponding predetermined magnitude of sensor current flow are defined.

Since current flows between the generator electrodes only so long as it is necessary to counteract the reduction in concentration of the titrating agent due to the presence of the reactive agent, the current flow in the generator circuit may be utilized to provide a direct measure of the concentration of reactive agent. Thus, the generator current flow through a resistor 35 in series with the generator electrodes may be sensed by a meter 37 to measure the concentration of the reactive agent. Since the reactive agent is continuously bubbling through the electrolytic solution to combine with the titrating agent, the measurement of concentration is on a continuous basis.

As will be described in connection with FIGURES 4 and 5, due to the structural arrangement of the generator electrode assembly 12 the titration cell 10 functions on a minimum of solution to respond rapidly to changes in concentration ranging from one hundredth part per million. Thus, the detection of generator current flow by the meter 37 provides a continuous measure of the concentration of the reactive agent which is sensitive to concentrations of the order of one hundredth part per million and responds rapidly to rapid changes in concentration of the reactive agent.

When the titration aparatus employs an extremely sensitive rapid acting relay as the switching means the titration apparatus as represented in FIGURE 1, need only include the titration cell 10, the sensor circuitry as shown, and the relay 28 and battery 24 connected in series with the generator electrodes for efficient operation. However, most commercially available relays are relatively slow acting and insensitive to small changes in sensor current from the predetermined magnitude.

To aid such relays to be rapid acting and responsive to small changes in current flow in the sensor circuit, the titrating apparatus of the present invention may take the form schematically represented in FIGURE 2 as including a transistor switch 37 in combination with a current limiting circuit 38. The transistor switch 37 includes a transistor 40 having an emitter 42 coupled to the generator electrode 14, a collector 44 coupled through a load resistor 46 to a negative terminal of the battery 24, and a base 48 coupled to the moveable contact 34 of the relay 28 and to a negative terminal of the battery 24 through a biasing resistor 50.

The current limiting circuit 38 includes a capacitor 52 coupled in a parallel circuit with a resistor 54 which is, in turn, connected in series with a blocking diode 56 between the generator electrode 16 and the base terminal 48 of the transistor 40. In this manner the current limiting circuit 38 shunts the moveable contact 34 and the contact 32 of the relay 28.

Due to the biasing provided by the battery 24 and the biasing resistor 50, the transistor 40 is in a conductive state when the relay 28 is open and is in a non-conductive state when the relay 28 is closed. Thus, initially when the polarizing film of hydrogen is present on the sensor electrode 18 to inhibit flow in the sensor circuit, the relay 28 is in its normally open state. With the relay 28 open, a current signal is pulsed from the battery 24 through the parallel circuit consisting of the capacitor 52 and the resistor 54 to begin to charge the capacitor 52 through the blocking diode 56. Current flow through the blockig diode 56 and the biasing resistor 50 in the base circuit 48 of the transistor 40 causes the transistor 40 to begin to conduct a current through its emitter-collector circuit and a current to flow between the generator electrodes 14 and 16. The current flow in the emitter-collector circuit is represented graphically in FIGURE 3 by the current signal rising as a function of time from time t_0.

Due to the series connection of the battery 24 between the generator electrodes, a small amount bromine (titrating agent) is generated at the generator electrode 16 and bubbled upward through the sensor electrodes. As previously described the bromine in contacting the sensor electrode 18 causes a depolarization of the polarized hydrogen film and results in an electrolytic reduction of the bromine at the sensor electrode 18 and a flow of current in the sensor circuit. The sensor current flows through the winding 30 of the relay 28, causing the relay 28 to close. The closing of the relay 28 by the moveable contact 34 impinging upon the contact 32 effectively short circuits the current limiting circuit 38 and connects the positive terminal of the battery 24 directly to the base circuit 48 of the transistor 40. This causes the transistor 40 to be instantaneously cut off as indicated in FIGURE 2 at time t_1 by the interruption of current flow in the emitter-collector circuit. In this manner, the battery 24 is effectively disconnected from the generator electrodes causing a cessation of bromine generation and allowing the capacitor 52 to discharge slowly through the resistor 54.

Although some of the bromine generated at the generator electrode 16 is electrolytically reduced at the sensor electrode 18, a like amount of bromine is developed at the sensor electrode 20. In this manner the sensor current flow does not cause a change in the bromine concentration in the solution which is normally maintained at a low predetermined level by the on-off operation of the relay 28. Accordingly, a current normally continues to flow in the sensor electrode circuit with a magnitude corresponding to the predetermined low level of bromine concentration. However, if the fluid being bubbled through the electrode assembly 12 contains a reactive agent which combines with bromine, the bromine concentration in solution is reduced. The reduction in bromine concentration is sensed by the sensor electrode circuit as a reduction in sensor current flow from the low predetermined magnitude. When the sensor current falls below that required to maintain the relay closed the

relay **28** returns to its normally open condition and the transistor **40** again becomes conductive in the manner described above allowing current to again flow in the emitter-collector circuit as represented at t_2 in FIGURE 3. The magnitude of current flow again increases until a time t_3 when the concentration of bromine in solutions exactly sufficient to compensate for the increase in concentration of the reactive agent.

Thus, due to the cooperative operation of the current limiting circuit **38** and the transistor switch **37**, a closing of the relay **24** in response to an initial increase in concentration of the reactive agent does not result in a sudden burst of high amplitude current flow in the generator circuit which might produce a generation of bromine much in excess of that required, thereby making the titration cell insensitive to small variations in reactive agent concentration which may immediately follow. Rather, a current signal is developed in the generator circuit which increases in magnitude until a sufficient concentration of bromine has been generated to compensate for the change in reactive agent concentration. This current limiting feature of the present invention is particularly important in providing for stable reference operation (blank operation) of the titration apparatus in the absence of the reactive agent in solution as well as maintaining the sensitivity of the apparatus to small changes in concentration which would be masked if unnecessarily large concentrations of bromine were generated.

The current limiting circuit and transistor switch combination further provides for rapid operation of the titration apparatus in response to rapidly occurring changes in concentration of the reactive agent. For example, in response to a first change in reactive agent concentration after the capacitor **52** has discharged (at the time t_2) the relay **28** immediately opens and current begins to flow from the battery **24** through the parallel RC network and the series diode **56**. Due to this current flow the capacitor begins to charge and a base current flows in the transistor **40** causing the transistor **40** to begin to conduct current in its emitter-collector circuit. The current in the emitter-collector circuit generates bromine in the manner described above to cause the relay **28** to again close. Upon the closing of the relay **28** the capacitor **52** is charged to a certain voltage level. Due to the blocking diode **56**, the capacitor **52** is prevented from rapidly discharging through the shunting path provided by the closed contacts **32** and **34** and slowly discharges through the resistor **54**. Thus, if the relay **28** is again immediately opened in response to another increase in reactive agent concentration substantially the same voltage is impressed across the resistor **54** causing substantially the same base current to flow in the transistor **40**. Accordingly, the transistor **40** returns instantaneously to the conductive condition present at the time t_3 as indicated as t_4 and continues to become more conductive as increasing current flows in the base circuit. As the transistor **40** becomes more conductive increasing amplitudes of current flow in the emitter-collector circuit. This process is continued with each rapidly occurring increase in concentration of the reactive agent until the capacitor **52** reaches a maximum charged condition at a time t_n. Henceforth, rapidly occurring changes in concentration of the reactive agent produce a maximum magnitude of current flow which may be sustained for a period of time required to generate sufficient bromine to again bring the solution to the predetermined level of bromine concentration.

Thus, due to the combination of the current limiting circuit **38** and the transistor switch **37** the relay **28** is sensitive to small changes in sensor current flow and operates to produce a generation of a much larger current flow in the generator circuit to rapidly counteract for rapidly occurring reductions in concentration of the titrating agent. In this manner the titrating apparatus of the present invention possesses an extremely rapid response time to small changes in concentration and possesses an exceptionally wide operating range.

As described, the generator current flow through the emitter-collector circuit of the transistor **40** is a pulsating on-off current. Since the magnitude of the generator current during each pulse increases until the bromine generated at the generator electrodes compensates for the concentration of the reactive agent present at that given time in the solution, the average amplitude of the generator current flow may be utilized as a measure of the concentration of reactive agent present in the solution. Thus, to provide a measure of the concentration of the reactive agent the pulsating current flow in the load resistor **46** is filtered through a filter represented at **58** to produce a voltage signal which is a representation of the average generator current flow. The voltage signal is measured by a recording meter **60**. For example, the meter **60** may be an electronic recording voltmeter which provides a continuous graphical record of the average current flow through the load resistor **56**.

To increase the accuracy and sensitivity of the measure of concentration by detecting the average value of generator current flow it has been found desirable to increase the frequency of operation of the relay **28** such that the relay opens and closes several times during each cycle of titrating agent concentration compensation. Thus, instead of being open until the concentration of titrating agent returns to the predetermined level the relay **28** opens and closes at a predetermined rate several times before the concentration of the titrating agent returns to the predetermined level. FIGURE 3 is a graphical representation of such operation. Such relay operation not only provides a more accurate average value of generator current but also eliminates any adverse effects of small noise signals from the sensing electrodes as well as hysteresis and "stricktion" of the relay **28**.

To provide such a rapid operation for the relay **28**, a negative feedback arrangement is coupled between a generator electrode and a sensor electrode of opposite polarity. Preferably the feedback connection is through a series resistor-capacitor network **62** which couples the generator electrode **14** to the sensor electrode **20**. In this manner when the relay **28** opens, current flow in the emitter-collector circuit of the transistor **40** is fed back to the sensor electrode **20** through the winding **30**, causing the relay **28** to again momentarily close. If the concentration of bromine in the solution has not returned to a level whereat sensor current flows in the sensor circuit, the relay immediately opens and the process is repeated. This effects a rapid turn-on and off of the relay to provide reproducible cycling between the on and off conditions of the relay.

The titration system of the present invention has been described including a general description of the generic features of the titration cell design of the present invention. For a more complete understanding of the titration cell design as well as the structural features which provide for continuous automatic titration, reference should be made to FIGURES 4 and 5.

Referring now to FIGURE 4, there is represented in cross-section one form of the rugged and compact titration cell design of the present invention which may be employed as the titration cell **10** in the automatic continuous titration apparatus represented in FIGURES 1 and 2.

The titration cell illustrated in FIGURE 4 is particularly adapted to the titration of substances such as sulfur compounds which are relatively insoluble in aqueous solutions. To provide such selective titration, the titration cell includes means for thoroughly mixing the sulfur compound with the solution to completely combine with the titrating agent in solution. In providing such sensitivity to difficult-to-dissolve substances, the cell illustrated in FIGURE 4 is relatively insensitive to substances which

are readily soluble in an aqueous solution—such substances rapidly hydrolyzing and not entering into the operation of the cell.

As represented in FIGURE 4, the titration cell includes a container 63 having an elongated end portion 64 and an adjacent end portion 66 having a volume which is less than that of the end section 64. The end section 66 is shaped in the form of a nipple having a valve arrangement 68 disposed therein for draining the container 63.

Included within end section 66 of the container 63 is an electrolytic solution represented at 69 containing ions of a titrating agent such as bromine. By way of example only, the electrolytic solution may be an aqueous acidified potassium bromide solution wherein bromide ions constitute the ions of the titrating agent bromine in solution.

Sealing the open end of the container 62 is a stopper member 70. To introduce the electrolytic solution into the container 63 a polyethylene tube 72 is disposed through the stopper 70 and extends into the container 63. Also disposed through the stopper 70 is a tube member 74. The tube member 74 may be composed of glass and extends longitudinally within the container 63 into the end section 66. Fused to the end of the tube 74 is a bubbler 76. Preferably the bubbler 76 is composed of sintered glass. Accordingly, a fluid pumped through the tube 74 diffuses through the pores in the sintered glass bubbler 76 and bubbles through the electrolytic solution 69 adjacent to the bubbler 76 to define a predetermined fluid path through the solution. Bubbles of the fluid including small amounts of the solution foam at the surface of the solution and rise in the container 63. In entering the end section 64, and due to the expanded volume thereof the bubbles burst and splatter against the sides of the container 63. The electrolytic solution which is carried with the bubbles drips down into the solution along the sides of the container 63 while the fluid in a gaseous state escapes through an outlet tube 78 which extends through the stopper 70.

As represented, the outlet tube 78 includes a diagonal slot 80 facing the stopper 70. Disposed within an end of the tube 78 is a material such as glass wool indicated at 82 allowing trapped electrolytic solution to drip back down into the end region 66 of the container 63.

In order to provide the electrolytic action of the titration cell described in connection with FIGURE 1, a compact electrode assembly 84 is mounted around the bubbler 76. The electrode assembly 84 comprises a pair of generator electrodes and a pair of sensor electrodes spaced in series along the path traversed by the fluid in bubbling through the electrolytic solution. The electrode assembly 84 includes a first generator electrode 86 which preferably takes the form of a coil of platinum wire wrapped around the bubbler 76 at a point just below the end of the tube 74. A second generator electrode 88 in the form of an open coil of platinum wire, is also wrapped around the bubbler 76 in an annular recess 90 which is disposed in the surface of the bubbler immediately above the end of the tube 74. Spaced from the generator electrodes are the pair of sensor electrodes 92 and 94. The sensor electrodes are preferably positioned above the solution level in the container 63 and operate by sensing the titrating agent which is foamed into contact therewith. The sensor electrode 92 may be composed of a platinum wire and is shaped in the form of an open coil around the bubbler and spaced approximately one-eighth inch from the generator electrode 88. The coil of the sensor electrode 92 may be approximately one-eighth inch in diameter to provide maximum contact with the foam. Spaced immediately adjacent to the sensor electrode 92 is the sensor electrode 94. The sensor electrode 94 is preferably composed of a platinum wire looped around the bubbler adjacent to the joint of the bubbler 76 with the tube 74.

Such a series arrangement of electrodes around the bubbler provides maximum electrode contact with the bubbling fluid and solution as well as sufficient spacing of sensor and generator electrodes to prevent electric fields generated by the generator electrodes from affecting the operation of the sensor electrodes. In particular, due to the series spacing of the generator and sensor electrodes a fluid pumped through the tube 74 bubbles through the bubbler 76 and contacts the generator electrode 88. The fluid then bubbles upward contacting the sensor electrodes 92 and 94 and is then emitted from the solution in the form of bubbles which rise upward toward the stopper 70.

The relative position of the bubbler, the sensor electrodes, and the solution level as described above, also maintains a uniform velocity of fluid flow in the region of the sensor electrode. This is of prime importance to the operation of the titration cell designs of the present invention for although the presence of the titrating agent in contact with the sensor electrodes depolarizes the hydrogen film on the first sensor electrode to produce a sensor current which is a function of the concentration of the titrating agent the ease of depolarization and hence the magnitude of sensor current flow is also a function of the fluid velocity past the sensor electrodes. Thus, since it is desired that the sensor current provide an accurate indication of only the titrating agent concentration, it is mandatory that the rate of fluid flow remain constant.

As described in connection with FIGURE 1, the generator and sensor electrodes are coupled to electrical circuitry external to the titration cell to produce electrical generation of the titrating agent at the generator electrodes and a sensing of the concentration of the titrating agent at the sensor electrodes. In order to provide such electrical connections a plurality of insulated electrical conductors 95 are included within the container 63. A conductor 95 is connected to each electrode and passes through a plastic tube 96 which is disposed through the stopper 70. Each conductor 95 is coupled to a terminal arrangement 97. The terminal 97 includes a plurality of electrical connectors 98 for plug-in connection to the external circuitry of FIGURE 1.

In this manner the sensor electrodes are coupled in series through a source of potential of the order of 0.5 volt and the generator electrodes are intermittently coupled in series through a source of potential of 3 or more volts. Thus, as described, a sensor current is developed in the circuitry coupled to the sensor electrodes which is a function of the concentration of the titrating agent in solution and provides means for controlling the generation of a current between the generator electrodes to be a direct measure of the concentration of the reactive agent.

Due to the combination of the bubbler 76 and electrode assembly 78 along the path of the fluid which is bubbled through the solution automatic continuous titration is provided by the titration cell.

Due to the compact bubbler-electrode assembly arrangement the continuous titration is provided in an extremely small volume of electrolytic solution. For example, the volume of electrolytic solution in the container 63 may be of the order of two milliliters or less. Thus, when changes occur in the concentration of the reactive agent being bubbled through the electrolytic solution a minimum of time is required for the generator electrodes to generate sufficient amounts of the titrating agent to return the sensor current to its predetermined level. This provides for continuous, automatic titration which is rapidly responsive to changes in concentration of the reactive agent.

Further, the bubbler-electrode arrangement operating on a small volume of electrolytic solution in combination with the circuitry of FIGURE 1 is highly sensitive to low concentrations of the reactive agent. For example, the titration cell, when utilized in a titration system such as described in connection with FIGURE 1, is capable of sensing concentrations of reactive agents down to one-one hundredth part in a million.

Referring to FIGURE 5 there is represented in cross-section a titration cell design of the present invention

which is particularly useful in titrating substances which are readily soluble in electrolytic solutions such as fuel vapors containing hydrazine and its derivatives. As is commonly known, hydrazine and its derivatives are compounds which hydrolyze in the presence of water or water vapor and react slowly with titrating agents such as bromine. Accordingly, it is desired to provide a cell design which allows a minimum of contact of a fluid containing hydrazine with the electrolytic solution (the cell therefore being insensitive to relatively insoluble substance such as sulfur compounds) and a maximum contact with the titrating agent. Such a cell structure is illustrated in FIGURE 5.

As represented, the titration cell includes a container **100** in which is disposed an electrolytic solution represented at **102**. The solution contains ions of a titrating agent such as bromine which combines with the hydrazine in known proportions to provide means for determining the concentration of hydrazine present in a fluid which is bubbled through the solution. Since hydrazine is readily soluble in electrolytic solution it may be desirable to utilize a solution having a low electrolyte concentration and hence a low conductivity. By way of example only, the electrolytic solution may be an aqueous solution comprising 3% potassium bromide, 5% sodium citrate, and ¼ of 1% citric acid.

As illustrated, the titration cell includes an outer tubular member **104** which may be composed of polyethylene type plastic. Disposed in one end of the tubular member **104** is a stopper arrangement **106**. The stopper **106** includes three adjacent annular sections **108**, **110** and **112** of decreasing radial dimension. The annular section **112** fits within an end of the outer tubular member **104**. The annular section **110** includes an annular slot and is dimensioned to fit within a top member **114** to seal the open top of the container **100**. Positioned within the annular slot **116** is an O-ring **118** which functions to provide an airtight seal between the stopper **106** and the top member **114**. The annular section **108** rests on the top member **114** to support the stopper member **106** and the outer tubular member **104** within the cell. The outer tubular member thus extends downward into the solution **102**, an open end **120** of the tubular member **104** being adjacent to the bottom of the container **100**.

Immediately above the open end **120** of the tubular member **104** is a slot indicated at **122** in the surface of the tubular member **104**. Due to the fluid which is pumped into the compartment defined by the tubular member **104** and the stopper **106** the solution **102** rises within the tubular member **104** to a point adjacent to the upper side of the slot **122**. As will be described in detail, this provides a limited but reproducible amount of electrolytic solution in the region of the electrode assembly of the titration cell for operation therewith.

Supported by the stopper and extending longitudinally within the tubular member **104** is a rod **124**. The rod **124** may be composed of Teflon and has an end member **126** having a concave lower face **128**. Preferably, as illustrated, the face **128** is cone shaped.

Mounted within the tubular member **104** is a sleeve member **130**. The sleeve member is preferably composed of a non-absorbent material such as Teflon and includes adjacent end sections **132** and **134**. The end section **132** has a larger volume than the end section **134**, and fits tightly around the circumference of the end member **126**. In this manner the end section **134** extends longitudinally within the tubular member **104** towards the bottom of the container **100**, and terminates above the open end **120**.

Disposed within an open end of the end section **134** is a glass plug member **136** having a bore **138** therein. Positioned within the bore **138** is a glass rod **140**. Due to capillary action, the surface of the glass rod **140** is wetted to provide a communicating path for the electrolytic solution into a chamber defined by the sleeve **130** and the end member **126**. Accordingly, the electrolytic solution **102** rises within the sleeve **130** to a level substantially even with the level of the solution within the tubular member **104**.

Mounted within the sleeve **130** is an inner tubular member **142**. The inner tubular member **142** may be composed of glass and extends longitudinally within the outer tubular member **104**. The inner tubular member **142** is fixedly positioned within the sleeve **130** by spacers such as indicated at **144** and **146** which provide a pressure fit between the inner tubular member **104** and the end section **134** of the sleeve **130**. In this manner the inner tubular member **142** is aligned with the sleeve **130** and spaced therefrom.

Disposed within the inner tubular member **142** is an electrode assembly **148**. As described briefly in connection with FIGURE 1, the electrode assembly **148** includes four electrodes spaced from each other along a path traversed by a fluid which is bubbled through the electrolytic solution. In this manner the fluid containing a reactive agent combines with the titrating agent in the region of a pair of generator electrodes to reduce the concentration of the titrating agent in the solution. The reduction in concentration of the titrating agent is sensed by the sensor electrodes through which the fluid and titrating agent are bubbled. The reduction in concentration of the titrating agent reduces a current flowing between the sensor electrodes to provide an indication of the amount of reactive agent present in the fluid.

To provide such operation in the titration cell represented in FIGURE 5, the electrode assembly **148** includes a first generator electrode **150** which preferably takes the form of a platinum wire coiled around the inner surface of the inner tubular member **142** adjacent to the plug **136**. Concentrically disposed within the first generator electrode is a second generator electrode **152** preferably taking the form of a platinum wire wound in an elongated coil extending toward the end section **126** and positioned adjacent to the plug **136**. Spaced above the generator electrodes **150** and **152** along the inner surface of the inner tubular member **142** is a first sensor electrode **154**. The sensor electrode **154** preferably takes the form of an elongated coiled platinum wire extending from a point immediately above the generator electrodes to the end of the inner tubular member adjacent to the end member **126**. Centrally disposed along the first sensor electrode and between a pair of coils of the first sensor electrode is a second sensor electrode **156** which takes the form of a single loop of platinum wire disposed around the inner surface of the inner tubular member **142**. Such an arrangement of electrodes provides maximum electrode contact with the bubbling fluid and solution as well as isolation of the second sensor electrodes from electric fields generated by the generator electrodes when connected to the external circuitry of FIGURE 1.

To provide means for connecting the generator and sensor electrode to electrical circuitry such as represented in FIGURE 1, electrical conductors represented at **158**, **150**, **162**, and **164** are included. The electrical conductors are enclosed in plastic tubes which extend through the stopper **106** to a terminal **166**. The terminal **166** includes a plurality of electrical contacts indicated at **168** to provide electrical plug-in connection for the electrodes to the externally located circuitry. The terminal **166** is fixedly attached to the stopper **106** by a screw member **170** and is covered by a plastic cap **172** which is attached to the stopper **106**.

As illustrated in one preferred form of the cell design of the present invention, portions of the conductors **164** and **158** adjacent to and connecting the generator electrodes to the terminal **170** are exposed to the solution external to the sleeve **130**. In this manner a small amount of bromine is generated in the outer volume of the solution to oxidize any residual unreacted reactive agent (hydrazine) which may pass into the outer volume of solution. Where such leakage of the reactive agent is a par-

ticular problem a larger portion of the generator electrode may be positioned external to the sleeve **130** or a separate coil arrangement in series with the generator electrodes may be provided.

To introduce the fluid containing unknown amounts of a reactive agent into the electrolytic solution of the titration cell, a tube **174** extends through a slot **176** in the stopper **106**, a slot **178** in the cap member **172**, downward into the outer tubular member **104** and into the sleeve **130** at a point between the plug **136** and the inner tubular member **142**. The end of the tube **174** is diagonally cut such that fluid is emitted in an upward direction through the inner tubular member **142**. The tube **174** is preferably composed of Teflon. In this manner an inlet is provided for the fluid which is resistant to plugging by fuel vapor and is a non-wetting arrangement for bubbling the fluid through the solution in the inner tubular member.

Due to the cooperating structural arrangement of the electrode assembly and the non-wetting bubbler, provided by the tube **174**, uniform velocity of fluid flow is maintained in the region of the sensor electrodes to insure that the sensor current is an accurate indication of the concentration of titrating agent in solution.

In operation, the generator electrode **152** is maintained at a positive potential relative to the generator electrode **150** and the sensor electrode **156** is maintained at a positive potential relative to the sensor electrode **154**. As described in connection with FIGURE 1, the titrating agent, bromine, is generated at the generator electrode **152**. The concentration of the titrating agent in the electrolytic solution within the inner tubular member **142** is sensed by the sensor electrodes **154** and **156** to produce a sensor current. A fluid is pumped through the tubing **174** into the sleeve **130** immediately below the inner tubular member **142**. In this manner, the fluid bubbles through the region of the generator electrodes within the inner tubular member **142** producing a complete combination of the reactive agent with the titrating agent in solution. This reduces the concentration of the titrating agent in solution in bubble form therewith. The titrating agent in ner tubular member carrying a portion of the electrolytic solution in bubble from therewith. The titrating agent in bubble form is electrolytically reduced at the sensor electrodes and the ions of the titrating agent are electrolytically oxidized at the second sensor electrode **156** to produce the sensor current. When a reduction occurs in the concentration of the titrating agent in solution, the sensor current falls from the predetermined magnitude thereby providing the operation of the titrating apparatus as described in connection with FIGURE 1.

The fluid and electrolytic solution in bubble form in passing from the inner tubular member **142** strike the concave surface **128** of the end member **126** causing the bubbles to burst. The electrolytic solution containing the titrating agent is splattered onto the inner surface of the sleeve **130** and drips downward between the sleeve **130** and the inner tubular **142** into the electrolytic solution within inner tubular member. The fluid in a gaseous state passes from a chamber defined by the sleeve **130** and the end member **126** through an opening **180** in the end section **132** of the sleeve **130**. The fluid expands in a chamber defined by the outer tubular member **104** in the stopper **106** to create a pressure in the chamber which maintains the level of the solution within the outer tubular member **104** at a point adjacent to the upper end of the opening **122**. The fluid then bubbles through the opening **122** and hence through the electrolytic solution **102** to the surface thereof. The fluid passes from the electrolytic solution **102** through an opening **182** in the top member **114** to the atmosphere.

The fluid in passing from the outer tubular member **104** through the opening **122**, causes a pumping action to occur which not only maintains a circulation of the electrolytic solution within container **100** and within the outer tubular member **104** but also allows electrolytic solution to be pumped through the plug **136** into the inner tubular member **142** to maintain the level of the electrolytic solution therein. In this manner controlled circulation of the electrolytic solution within the titration cell is provided to maintain uniform electrolytic concentration with the solution.

As described above, the pressure within the chamber defined by the outer tubular member **104** and the stopped **106** in conjunction with the fluid being pumped therethrough maintains the level of the solution within the outer tubular member **104** adjacent to the upper side of the opening **122**. In this manner, only a small amount of electrolytic solution (less than one milliliter) is exposed to the operation of the titration cell at any one time. As described above, this provides for rapid response of the titration cell to changes in the concentration of the reactive agent in that only small amounts of the titrating agent need be generated to compensate for changes in the concentration of the reactive agent being bubbled throug the cell.

Thus, the titration cell represented in FIGURE 5 provide means for continuously and automatically detecting concentrations of reactive agents present in a fluid and through a cooperation of its electrode assembly and the outer tubular member operates on a small quantity of electrolytic solution to provide a titration cell which responds rapidly to changes in the concentration of a reactive agent being bubbled through the cell. Therefore, the titration cell represented in FIGURE 5 is ideally suited for use in the detection of less than dangerous concentrations of noxious vapors such as hydrazine and its derivatives present in the handling of high propellant fuels.

Although the cell structures have been described as operating in a small volume of electrolytic solution, the titration cells also provide excellent operation in larger volumes of solution where rapid response to changes in the concentration of the reactive agents is not required. Thus, although the cell structure of FIGURE 4 has been described in connection with a container having an end portion of reduced volume in the region of the electrode assembly, the cell will function as described in a larger container such as represented in FIGURE 5. Also, to provide a small volume of electrolytic solution in the region of the electrode assembly, the outer tubular member mixing arrangement described in connection with FIGURE 5, may be utilized in combination with the bubbler electrode assembly of FIGURE 4 to replace or supplement the dump and refill valve arrangement. Further, it is to be understood that the electrode assembly of FIGURE 5, although described in conjunction with the outer tubular member arrangement, may be utilized in a container such as represented in FIGURE 4.

What is claimed is:

1. Continuous amperometric titration apparatus comprising: means defining a titrating cell having a pool of electrolytic solution disposed therein, the solution containing an excess of ions of a titrating agent; means including a bubbler for continuously introducing a gas having unknown amounts of a reactive agent into the electrolytic solution to combine with and reduce the concentration of the titrating agent in solution; means for constraining the gas to follow a predetermined gaseous path through the electrolytic solution; an electrode assembly, positioned in said titrating cell, and in said predetermined gaseous path, for the generation of the titrating agent from the electrolytic solution and for the sensing of the concentration of the titrating agent in solution including a first generator electrode, a second generator electrode closely spaced from the first generator electrode along said predetermined gaseous path, a first sensor electrode spaced from the second generator electrode along said gaseous path, and

a second sensor electrode closely spaced from the first sensor electrode along said gaseous path, the first and second generator electrodes being immediately adjacent the first and second sensor electrodes and each electrode being unshield from the other electrodes; means for developing a potential difference between the first and second generator electrodes such that the titrating agent is electrolytically formed from the electrolytic solution at the second generator electrode; means for developing a potential difference between the first and second sensor electrodes which is insufficient to generate hydrogen from the solution and which causes electrolytic reduction of the titrating agent to occur at the first sensor electrode and electrolytic oxidation of the ions of the titrating agent to occur at the second sensor electrode when the titrating agent generated at the generator electrode passes with the gas into contact with the sensor electrodes, the electrolytic reduction and oxidation at the sensor electrodes producing a current flow between the first and second sensor electrodes which is a function of the concentration of the titrating agent in solution; means for controlling the amount of electrolytic formation of said titrating agent, from said pool of electrolytic solution, in response to said current flow between said first and second sensor electrodes; means for measuring the average current flow between said first and second generator electrodes; and means for replenishing said pool with additional electrolytic solution.

2. Continuous amperometric titration apparatus comprising: a vessel containing a pool of electrolytic solution, the solution containing an excess of ions of a titrating agent; means including a bubbler for continuously bubbling a gas having unknown amounts of a reactive agent through the electrolytic solution along a predetermined gaseous path to combine with and reduce the concentration of the titrating agent in solution; an electrode assembly including a first generator electrode mounted around the bubbler at one end thereof, a second generator electrode mounted around the bubbler and spaced along the bubbler closely adjacent the first generator electrode such that gas passing from the bubbler and rising toward the surface of the solution enters a region of the first generator electrode prior to contacting the second generator electrode, a first sensor electrode mounted around the bubbler and spaced from the second generator electrode downstream from the first generator electrode, a second sensor electrode mounted around the bubbler closely adjacent to the first sensor electrode and downstream from the second generator electrode; the first and second generator electrodes being immediately adjacent the first and second sensor electrodes and each electrode being unshielded from the other electrodes; means for generating the titrating agent from said pool at the second generator electrode; means for developing a potential difference between the first and second sensor electrodes and which causes electrolytic reduction of the titrating agent to occur at the first sensor electrode and electrolytic oxidation of the ions of the titrating agent to occur at the second sensor electrode when the titrating agent generated at the second generator electrode is bubbled with solution and the gas into contact with the sensor electrodes, the electrolytic reduction and oxidation producing a current flow between the first and second sensor electrodes which is a function of the concentration of the titrating agent in solution; means for sensing said current flow between the sensor electrodes; means for controlling the amount of electrolytic formation of said titrating agent, from said pool of electrolytic solution, in response to said current flow between said first and second sensor electrodes; means for measuring the average current flow between said first and second generator electrodes; and means for replenishing said pool with additional electrolytic solution.

3. Continuous amperometric titration apparatus comprising: means defining a titrating cell having a pool of electrolytic solution disposed therein, the solution containing a large excess of ions of a titrating agent; means including a bubbler for continuously bubbling a gas having unknown amounts of a reactive agent into the solution to combine with and reduce the concentration of the titrating agent in solution; means for constraining the gas to be bubbled along a predetermined gaseous path through the solution to cause the reactive agent to completely combine with the titrating agent; a first generator electrode positioned in the predetermined gaseous path; a second generator electrode spaced from and immediately adjacent to the first generator electrode and positioned along the predetermined gaseous path; a first sensor electrode spaced from the second generator electrode along the predetermined gaseous path; a second sensor electrode spaced from and immediately adjacent to the first sensor electrode along the predetermined gaseous path, the first and second generator electrodes being immediately adjacent the first and second sensor electrodes and each electrode being unshielded from the other electrodes; a source of potential; switching means for coupling the source of potential between the first and second generator electrodes to cause a current to flow between the generator electrodes and oxidation of the ions of the titrating agent to occur at the second generator electrode to form the titrating agent from the solution, the titrating agent being bubbled into contact with the sensor electrodes; means for maintaining the first sensor electrode at a predetermined potential relative to the second sensor electrode which is less than that required to generate hydrogen from the solution such that electrolytic reduction of the titrating agent occurs at the first sensor electrode and electrolytic oxidation of the ions of the titrating agent occurs at the second sensor electrode when said gas containing titrating agent is bubbled into contact with the sensor electrodes, the electrolytic reduction and oxidation causing a current flow between the first and second sensor electrodes which is a function of the concentration of the titrating agent in solution; means responsive to the current flow between the sensor electrodes for controlling the switching means to couple the source of potential to the generator electrodes only when the current flowing between the sensor electrodes reaches a predetermined value; means for sensing the current flow between the generator electrodes and means for replenishing said pool with electrolytic solution.

4. A continuous amperometric titration assembly comprising: a vessel containing a pool of electrolytic solution, the solution containing a large excess of ions of a titrating agent; means for introducing a gas having unknown amounts of a reactive agent into the electrolytic solution to combine with and reduce the concentration of the titrating agent in solution; means for constraining the gas to bubble along a predetermined gaseous path through the solution; means for withdrawing the gas from the container after the gas has passed through the electrolytic solution; an electrode assembly positioned in the container along siad predetermined gaseous path to generate the titrating agent from the electrolytic solution and to sense the concentration of the titrating agent in solution including a first generator electrode positioned in said predetermined gaseous path, a second generator electrode spaced from, and immediately adjacent to, the first generator electrode along said predetermined gaseous path, a first sensor electrode spaced from the second generator electrode along said predetermined gaseous path, and a second sensor electrode spaced from, and immediately adjacent to, the first sensor electrode along said predetermined gaseous path downstream from the generator electrodes, the first and second generator electrodes being immediately adjacent the first and second sensor electrodes and each electrode being unshielded from the other electrodes; a first source of potential coupled between the sensor electrodes to maintain the first sensor electrode negative relative to the second sensor

electrode and produce a polarizing film of hydrogen on the second sensor electrode which inhibits current flow between the sensor electrodes, the polarizing film being depolarized by the presence of the titrating agent in the region of the sensor electrodes to cause electrolytic reduction of the titrating agent to occur at the first sensor electrode, electrolytic oxidation of the ions of the titrating agent to occur at the second sensor electrode, and a current to flow between the sensor electrodes which is a function of the concentration of the titrating agent in solution; a second source of potential; a transistor having an emitter-collector circuit and a base circuit, the emitter-collector circuit being connected in series with the second source of potential and the first and second generator electrodes; a normally open relay responsive to the current flow between the sensor electrodes to close and couple the base circuit of the transistor to the second generator electrode; means for biasing the transistor from the second source of biasing potential to be conductive when the relay is open to connect the second source of potential in series between the generator electrodes and cause electrolytic oxidation of the ions of the titrating agent to occur at the second generator electrode and a current to flow between the generator electrodes through the emitter-collector circuit; a resistor and a capacitor connected in a parallel circuit and in series with a diode between the base circuit of the transistor and the second generator electrode to shunt the relay, the diode being poled for series current flow from the second source of potential to the base circuit to provide a current controlled circuit for the relay; and means for sensing the current flow in the emitter-collector circuit of the transistor.

5. The apparatus defined in claim 4 including negative feedback means coupled between the first generator electrode and the second sensor electrode.

6. A continuous amperometric titration cell comprising: means defining a titrating compartment having an electrolytic solution disposed therein, the solution containing an excess of ions of a titrating agent; means for introducing a gas containing a reactive agent into the electrolytic solution including a tubular member extending from outside the titrating compartment into the solution, the tubular member being terminated in a glass bubbler such that a gas introduced into the tubular member is bubbled through the glass bubbler and rises in the solution around the tubular member to define a path of gaseous flow; means for withdrawing the gas from the titrating compartment after it has bubbled to the surface of the solution; an electrode assembly positioned within the titrating compartment for generating the titrating agent from the solution and sensing the concentration of the titrating agent in solution including a first generator electrode wound around an end of the bubbler adjacent to the bottom of the chamber, a second generator electrode wound around the bubbler immediately adjacent the first generator electrode along the path of gaseous flow, a first sensor electrode wound around the bubbler along the path of gaseous flow spaced from the second generator electrode, and a second sensor electrode wound around the bubbler immediately adjacent to the first sensor electrode downstream from the generator electrodes, the first and second generator electrodes being immediately adjacent the first and second sensor electrodes and each electrode being unshielded from the other electrodes; means for coupling the generator electrodes to a first source of potential such that the titrating agent is generated from the ions in solution to be bubbled with the gas into contact with the sensor electrodes; means for coupling the sensor electrodes to a second source of potential such that electrolytic reduction of the titrating agent occurs at one of the sensor electrodes, an electrolytic association of the ions of the titrating agent occurs at the other sensor electrode, and a current flows between the sensor electrodes which is a function of the concentration of the titrating agent in solution; means for controlling the amount of electrolytic formation of said titrating agent, from said pool of electrolytic solution, in response to said current flow between said first and second sensor electrodes; and means for measuring the average current flow between said first and second generator electrodes.

7. The apparatus defined in claim 6 wherein the bubbler is a sintered glass bubbler.

8. In a continuous amperometric titration cell having means for continuously bubbling a gas containing a reactive agent along a predetermined gaseous path through pool of an electrolytic solution containing a large excess of ions of a titrating agent, an electrode assembly for generating the titrating agent from the electrolytic solution and sensing the concentration of the titrating agent in solution comprising a first generator electrode positioned in said predetermined gaseous path, a second generator electrode closely spaced from the first generator electrode along said predetermined gaseous path, means coupling the first and second generator electrodes for generating the titrating agent from the ions at one of said generator electrodes, the titrating agent being bubbled with said gas along said predetermined gaseous path to combine with the reactive agent, a first sensor electrode spaced from, and immediately adjacent to, the second generator electrode along said predetermined gaseous path, a second sensor electrode immediately adjacent to the first sensor electrode and spaced along said predetermined gaseous path downstream from the generator electrodes, the first and second generator electrodes being immediately adjacent the first and second sensor electrodes and each electrode being unshielded from the other electrodes; means for maintaining a potential difference between the first and second sensor electrodes to cause electrolytic reduction of the titrating agent to occur at one of the sensor electrodes, electrolytic oxidation of the ions of the titrating agent to occur at the other sensor electrode, and a current to flow between the sensor electrodes which is a function of the instantaneous concentration of the titrating agent in solution; means for controlling the amount of electrolytic formation of said titrating agent, from said pool of electrolytic solution, in response to said current flow between said first and second sensor electrodes; means for measuring the average current flow between said first and second generator electrodes; and means for replenishing said titration cell with additional electrolytic solution.

9. A continuous amperometric titration cell for use in a continuous titration apparatus comprising: means defining an open top container having an electrolytic solution disposed at the bottom thereof, the solution containing ions of a titrating agent; stopper means for sealing the top of the container; an outer tubular member coupled to the stopper to extend longitudinally toward the bottom of the container, the outer tubular member having a hole in its outer surface near an open end adjacent to the bottom of the container; a rod supported by the stopper to extend longitudinally within the outer tubular member; a tubular sleeve having first and second end portions, the first end portion being mounted tightly around the end of the rod and having a volume which is greater than the volume of the second end portion, the first end section also having a hole in its outer surface; a plug inserted into the second end portion of the sleeve for admitting controlled amounts of the solution within the sleeve; an inner tubular member longitudinally mounted within and laterally spaced from the sleeve, one end of the inner tubular member being adjacent to the plug and the other end of the inner tubular member being adjacent to the end of the rod; a length of tubing extending into the second end portion of the sleeve between the inner tubular member and the plug for bubbling a fluid containing unknown amounts of a reactive agent into the inner tubular member; an electrode assembly mounted within the inner

tubular member and including a first generator electrode in the form of an elongated coil of wire extending longitudinally along the inner surface of the inner tubular member adjacent to the plug, a second generator electrode in the form of an elongated coil of wire closely spaced to and mounted concentrically within said first generator electrode, a first sensor electrode in the form of an elongated coil of wire extending longitudinally along the inner surface of the inner tubular member from a point spaced from the first generator electrode to the end of the inner tubular member adjacent to the rod, and a second sensor electrode in the form of a wire looped around the inner surface of the inner tubular member and spaced between a pair of coils of said first sensor electrode in close relationship therewith; means for coupling the first and second generator electrodes to a first source of potential; means for coupling the first and second sensor electrodes to a second source of potential to cause the titrating agent to be generated by the generator electrodes, and a current to flow between the sensor electrodes which is a function of the concentration of the titrating agent in solution; means for controlling the amount of electrolytic formation of said titrating agent, from said pool of electrolytic solution, in response to said current flow between said first and second sensor electrodes; and means for measuring the average current flow between said first and second generator electrodes.

10. The apparatus defined in claim **9** wherein the rod includes an end member extending into the sleeve having a concave-like surface facing the inner tubular member.

11. The apparatus defined in claim **9** wherein the plug is of glass and has a slot therein into which is positioned a glass rod to provide a wetted communicating path for the solution into the sleeve.

12. The apparatus defined in claim **9** wherein the second source of potential develops a voltage of less than **0.5 volt.**

13. A continuous amperometric titration cell for use in a continuous titration apparatus, comprising: means defining a chamber having an electrolytic solution disposed therein, the solution containing ions of a titrating agent; a tubular member longitudinally mounted within the chamber such that a portion of the tubular member is immersed in the solution; an electrode assembly mounted within the tubular member including a first generator electrode taking the form of an elongated coil of wire extending longitudinally along an inner surface of the tubular member and immersed in the solution, a second generator electrode taking the form of an elongated coil of wire closely spaced to and mounted concentrically within said first generator electrode, a first sensor electrode taking the form of an elongated coil of wire extending longitudinally along the inner surface of the tubular member from a point spaced from the first generator electrode, a second sensor electrode in the form of a loop of wire mounted around the inner surface of the tubular member and spaced between a pair of coils of said first sensor electrode in close relationship therewith; means for extending a portion of the generator electrodes beyond the tubular member; means for coupling the generator electrodes to a first source of potential such that a current flows between the generator electrodes to generate the titrating agent from solution; means for coupling the sensor electrodes to a second source of potential such that a current flows between the sensor electrodes which is a function of the concentration of the titrating agent in solution; and means for bubbling a fluid containing unknown amounts of a reactive agent into the chamber such that the fluid bubbles along a path defined by the tubular member to cause a combination of the reactive agent and the titrating agent to occur in the region of the generator electrodes and a reduction in the current flow between the sensor electrodes to occur which is a function of the concentration of the reactive agent in the fluid; means for controlling the amount of electrolytic formation of said titrating agent, from said pool of electrolytic solution, in response to said current flow between said first and second sensor electrodes; and means for measuring the average current flow between said first and second generator electrodes.

14. Continuous amperometric titration apparatus comprising: means defining a chamber including a small quantity of aqueous electrolytic solution disposed therein, the solution containing a large excess of ions of a titrating agent; means for continuously bubbling a gas containing a reactive agent along a predetermined gaseous path through the solution; a compact electrode assembly positioned in said predetermined gaseous path and comprising first and second generator electrodes closely spaced along said predetermined gaseous path and first and second sensor electrodes closely spaced along said predetermined gaseous path, the first and second generator electrodes being immediately adjacent the first and second sensor electrodes and each electrode being unshielded from the other electrodes; means coupled to the generator electrodes for developing a current signal between the generator electrodes to generate the titrating agent from the ions at one of the generator electrodes; means coupled to the sensor electrodes for generating a current signal between the sensor electrodes which is a function of the concentration of the titrating agent in the solution; and means responsive to the current signal between the sensor electrodes for controlling the means for generating a current signal between the generator electrodes such that a current is generated between the generator electrodes only when the current signal between the sensor electrodes falls to a predetermined value; means for sensing the current flow between generator electrodes, and means for replenishing said chamber with additional aqueous electrolytic solution.

15. A process for the continuous amperometric titration of an unknown amount of a substance which substance is reactive to a titrating agent, comprising the steps of:

continuously bubbling a gas, having unknown amounts of said substance to be measured, at a substantially fixed rate, into a first region of a pool of electrolytic solution containing ions of a titrating agent;

providing a potential between a first pair of closely spaced electrodes disposed in said first region to electrolytically form titrating agent, in situ, in said first region of said pool of electrolytic solution, whereby said titrating agent and said substance are reacted;

passing the gas with any unreacted titrating agent into a second region;

providing a potential between a second pair of closely spaced electrodes disposed in said second region to electrolytically reduce and then electrolytically oxidize any unreacted titrating agent thereby producing a current flow, said first pair of electrodes being immediately adjacent said second pair of electrodes and each electrode being unshielded from the other electrodes;

controlling the amount of electrolytic formation of said titrating agent, in situ, from said pool of electrolytic solution in response to said current flow;

measuring the average current flow between said first pair of electrodes; and

periodically replenishing said pool of electrolytic solution.

16. A process for the continuous amperometric titration of a substance to be measured, which substance is reactive to a titrating agent, comprising the steps of:

continuously bubbling a gas, having unknown amounts of said substance to be measured, at a substantially fixed rate, into a first region of a pool of electrolytic solution containing ions of a titrating agent;

providing a potential between a first pair of closely spaced electrodes disposed in said first region to electrolytically form titrating agent, in situ, in said first region of said pool of electrolytic solution, whereby said titrating agent and said substance are reacted;

passing the gas with any unreacted titrating agent into a second region;

providing a potential between a second pair of closely spaced electrodes disposed in said second region to reduce and then oxidize electrolytically any unreacted titrating agent and thereby producing a current flow, said first pair of electrodes being immediately adjacent said second pair of electrodes and each electrode being unshielded from the other electrodes;

controlling the amount of electrolytic formation of said titrating agent, in situ, from said pool of electrolytic solution in response to said current flow;

measuring the average current flow between said first pair of electrodes;

separating said electrolytic solution entrained in said gas leaving said second region from said gas, and returning said electrolytic solution into said pool to thereby recirculate said electrolytic solution; and

replenishing said pool with additional electrolytic solution containing ions of said titrating agent.

17. A process for the continuous amperometric titration of a substance to be measured, which substance is reactive to a titrating agent, comprising the steps of:

continuously bubbling a gas, having unknown amounts of said substance to be measured, at a substantially fixed rate, into a first region of a pool of electrolytic solution containing ions of a titrating agent;

providing a potential between a first pair of closely spaced electrodes disposed in said first region to electrolytically form titrating agent, in situ, in said first region of said pool of electrolytic solution, whereby said titrating agent and said substance are reacted;

passing the gas with any unreacted titrating agent into a second region;

providing a potential between a second pair of closely spaced electrodes disposed in said second region to electrolytically reduce any unreacted titrating agent

and then electrolytically oxidizing ions of said unreacted titrating agent thereby producing a current flow, said first pair of electrodes being immediately adjacent said second pair of electrodes and each electrode being unshielded from the other electrodes;

controlling the amount of electrolytic formation of said titrating agent, in situ, from said pool of electrolytic solution in response to said current flow;

measuring the average current flow between said first pair of electrodes; and

replenishing said pool with additional said electrolytic solution.

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