Dec. 22, 1964 D. D. DE FORD ETAL 3,162,585

CONTINUOUS AUTOMATIC COULOMETRIC TITRATION SYSTEM

Filed April 12, 1960 2 Sheets-Sheet 1

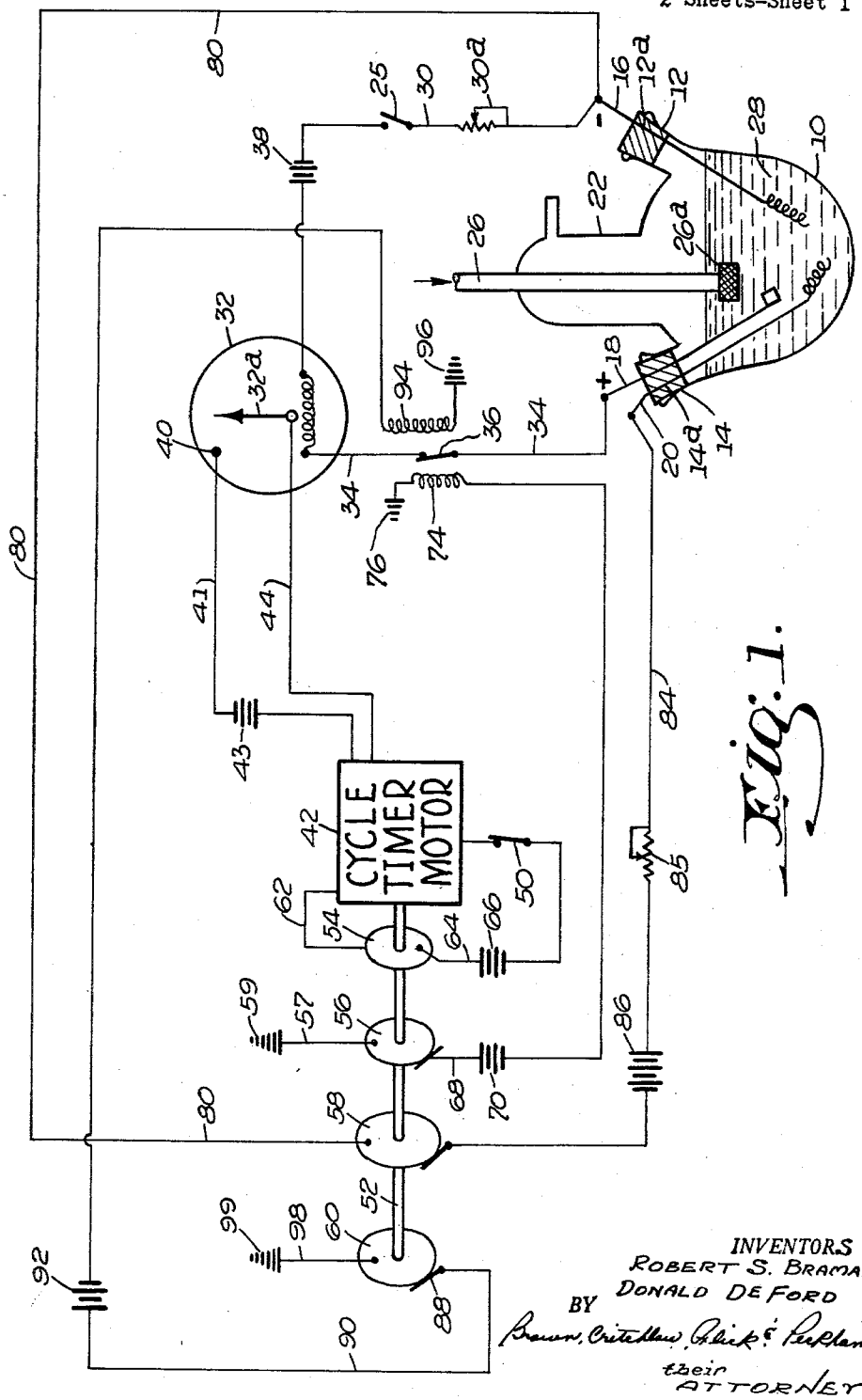


Fig. 1.

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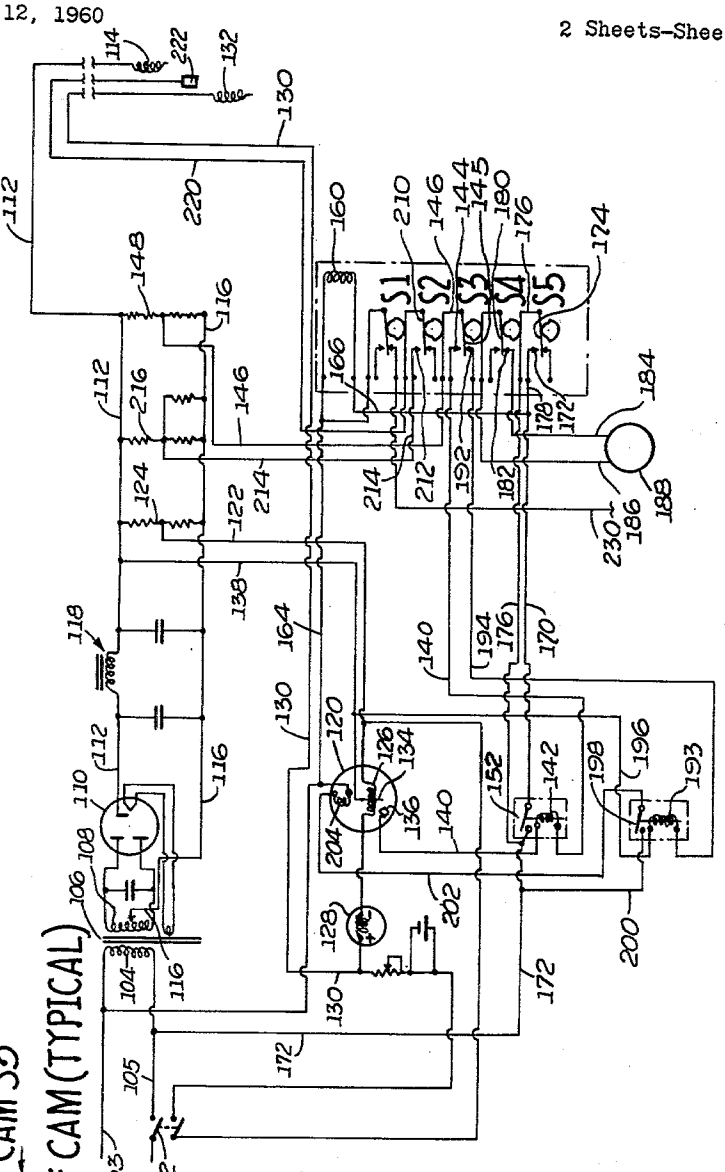


Fig. 2.

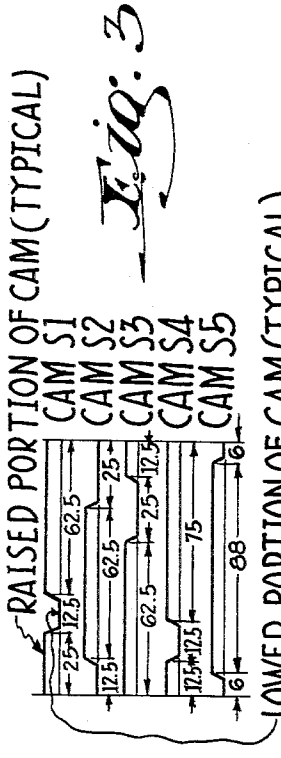


Fig. 3.

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CONTINUOUS AUTOMATIC COULOMETRIC TITRATION SYSTEM

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5 Claims. (Cl. 204—1)

This invention relates to a continuous automatic coulometric titration system and in particular it concerns such a system that is of particular usefulness with respect to monitoring an atmosphere for the presence of small concentrations of such materials as the boranes.

Because of their toxicity and volatility, the presence of the boron hydrides in an atmosphere constitutes a safety hazard to personnel working there. The maximum allowable concentrations of diborane, pentaborane and decaborane, respectively, have been set at 0.1, "as near to zero as possible," and 0.05 p.p.m. (volume). Since an adequate safety program requires analyzing air for low concentrations of boranes, the analytical problems involved have been studied by artisans in this field.

Several methods for determining boron hydrides (boranes) in air or gas mixtures have been reported. Some have involved the conversion of the borane, after its withdrawal in a suitable gas sample, to boric acid and then applying normal analysis procedures thereto. Boric acid has been determined by both microtitration and coulometric techniques. Ultraviolet spectrophotometric methods have been reported for detecting decaborane; the disadvantage of this procedure is that it does not detect pentaborane or diborane or alkyl derivatives of those compounds. Coulometric detection systems for decaborane have also been proposed. Other systems have been suggested in which tetrazolium salts have been reacted with the boranes.

The foregoing methods of detection have certain limitations. For example, either their sensitivity is inadequate in view of the standards that have been applied, or they are tedious, subject to material interference or otherwise are not suitable. Other systems are undesirable in view of the fact that they can be used to detect the presence of but a single borane.

It is therefore an object of the present invention to provide a continuous automatic coulometric titration system, particularly useful for the detection of boranes in very small concentrations, that is reliable; that is simple; that has high sensitivity; and that is easy to operate with routine skills available in the art.

In accordance with the present invention, atmosphere monitoring is carried out by continuously passing samples from the atmosphere through a solvent-electrolyte that absorbs the material to be detected. The absorbing liquid contains a component that, upon electrolysis thereof, yields a material that will react quantitatively with the material to be detected. Sensing means are applied to the solvent electrolyte to monitor the concentration of the material released by electrolysis and, when that concentration falls below a predetermined value, to initiate generation of that electrolysis product. Release of the electrolysis product is proportional to the quantity of electricity passed through the solvent-electrolyte. Accordingly, upon applying a predetermined current for a prescribed period of time, the total quantity of electrolysis product is indicated. By noting the number of cycles of generation, each being responsive to a need as just defined, the consumption of the electrolysis reaction product is established as is the quantity of material being detected. In this general manner, we are able to detect the presence

of, for example, boranes in air or gas mixtures when they are present in very small concentrations in a manner whereby a continuous record of the concentration is immediately available to the atmosphere monitor.

The invention will be most readily understood upon considering its description in conjunction with the attached drawings in which:

FIG. 1 represents a more or less diagrammatic form of an embodiment of the invention showing a combined reaction indication vessel, associated circuitry and mechanical linkages by which the invention may be practiced;

FIG. 2 is a detailed electrical diagram showing an embodiment of controlling means operative from an A.C. power source, that can be associated with a titrometric vessel, such as that of FIGURE 1, in practicing the invention; and

FIG. 3 shows, diagrammatically, the cam surface characteristics of the cams in the microswitches of FIGURE 2.

Referring now to FIG. 1, the numeral **10** indicates a vessel in which the amperimetric titration is to occur. In the embodiment shown, this comprises a conventional flask having arm portions **12** and **14** stoppered by nonconducting corks **12***a* and **14***a* through which extend electrodes **16**, **18** and **20**. The electrodes in this embodiment all are composed of platinum, but it will be apparent that other materials inert to the electrolyte can be used as well. A central neck portion **22** having an outlet port **24** near its upper end is provided for adding electrolyte as desired. A tube **26** extending through neck portion **22** and terminating in a screen member **26***a* below the surface of an electrolyte **28** is used to introduce a gas to stir the electrolyte during operation. Other stirring means can be used if desired.

The titration vessel is completed by an electrolyte **28**. The electrolyte chosen, of course, depends upon the material being detected. In general, however, suitable electrolytes are characterized in that they will absorb the component being detected without very rapidly bringing about deleterious reactions therewith. For example, in the instance of boranes, the electrolyte must not hydrolyze the borane more rapidly than it can be detected. Another characteristic of the electrolyte is that upon the passage of an unidirectional current through it, it will generate a material that rapidly reacts with the substance being detected. Again in the instance of boranes, an iodide salt such as potassium iodide can be used and upon the passage of electric current therethrough free iodine is released. Free iodine rapidly reacts with boranes such as diborane, pentaborane and decaborane.

Electrode **16** comprises a cathode and is common to the two circuits that depend upon the electrolyte as a component thereof. A lead **30** from the cathode through a master switch **25**, a battery **38**, to one terminal of a microammeter **32** and a second lead **34**, from anode **18** through a switch **36**, that is normally closed, which lead is connected to a second terminal of the indicating microammeter **32**, comprise a first or indicating circuit, and it is, operatively, an amperimetric circuit. A variable resistor **30***a* in lead **30** is provided to permit adjustment of the indication current as desired. The ammeter **32** is provided with a contact **40** that the pointer **32***a* of the ammeter **32** can reach and touch. This contact is connected through lead **41** to an actuation mechanism, i.e., D.C. current source **43**, of a motor **42**. Another lead **44** extends through the pointer of the microammeter **32** to the other terminal of the power source of motor **42**.

Motor **42** operates a shaft **52** on which are four cams **54**, **56**, **58** and **60**. All of these cams are shown diagrammatically. The first of these cams **54** has a first lead **62** in contact with the motor and a second lead **64** that upon rotation of the cam completes the circuit through

said first lead through motor 42 through a normally closed switch 50 and through a power source indicated by the battery 66. A counter, not shown, is operatively associated with cam 54 to record the number of complete cycles it makes.

The second cam 56 is so characterized as to make contact with a lead 68 upon partial rotation thereof but only after cam 54 closes its circuit. Lead 68 connects through a battery 70 to the coil 74 of an electromagnet and finally to ground 76. The coil 74 is in operative relationship with the switch 36 hereinbefore mentioned in the lead 34 to microammeter 32. The remainder of the circuit of this cam 52 comprises a lead 57 to a ground 59.

The third cam 58 has a permanent contact against one side thereof which leads to the cathode 16 through a suitable electric lead 80. A second contact 82, adapted to be operated upon rotation of the cam, extends through an electrical lead 84 to a power source 86 and then to an anode 20 in the titrometric vessel 10 hereinbefore mentioned. A variable resistor 85 in lead 84 is provided to adjust the generation current to the desired level. The characteristics of this cam are adapted to close the circuit described in connection with cam 56.

The fourth cam 60 is so characterized that it closes a circuit comprising a contact 88, a lead 90, a power source 92, a coil 94 of an electromagnet and a ground connection 96. The coil 94 is of a size, strength and location to oppose the effects of the coil 74 hereinbefore mentioned and close switch 36 upon closing of the circuit of which coil 94 is a part. The characteristics of cam 60 are such that this circuit actuates only after the opening or inactivation of the circuit that is associated with the cam 58. The circuit of cam 60 is completed through a lead 98 to a ground 99.

In operation of this device, a sample of air or liquid suspected of containing the material that is to be detected is provided, as by being pumped through inlet tube 26 of the titrometric vessel 10. The master switch 25 hereinbefore mentioned is closed. This closes the circuit comprising cathode 16, anode 18, indicating microammeter 32 and power source 38. As a consequence of the previous setting of the contact 40 in microammeter 32, if the concentration of the agent in the electrolyte 28 is above the level indicated by contact 40, the titration can be carried out. If the level of that active component is below the pre-set value, the pointer 32*a* will make contact with contact member 40 thereby closing a circuit through leads 41 and 44 to the motor 42. The closing of that circuit will actuate the motor 42 and its shaft 52 upon which the cams, hereinbefore mentioned, are mounted.

All of the cams naturally rotate but because of their predetermined shape and surface characteristics, they close or open the respective circuits associated therewith in a predetermined sequence. Cam 54, upon rotation, closes a circuit that includes leads 62 and 64, a power source 66 and a switch 50, that is normally closed, that locks on power to the motor so that it will stay on until that cam has made a full rotation and comes to the open position. Of course, the size of the cam and the speed of the rotation can be pre-set to make the length of any given cycle a predetermined value.

Shortly after the motor is locked-on, the cam 56 closes the circuit which includes lead 68, power source 70 and the coil 74. The energization of this coil, as with any electromagnet, attracts the arm of switch 36 thereby breaking the indicating circuit of which switch 36 and the milliammeter 32 is a part. This frees the pointer so that at the end of a generation cycle, hereinafter described, it can indicate the concentration of the active component in the cell.

Shortly after the indicating switch circuit is broken as just indicated, cam 58 makes contact with member 82 thereby closing the circuit that includes lead 84, power source 86, anode 20 and lead 80 and cathode 16. This passes current through the electrolyte 28 in the titrometric vessel 10 thereby generating a quantity of, in the instance of potassium iodide, iodine that is proportional to the current value in that circuit and the time that the circuit is closed. This point is well understood by the artisan and, of course, comprises coulometric generation of the indicating agent. By sizing the cam and setting the time per cycle in which its circuit is closed, the quantity of iodine generated is predetermined and can be recorded.

In the embodiment shown, at the end of the predetermined generation circuit, the generation circuit is automatically opened. This occurs through the cam having returned to the original position in which the circuit is open. Once cam 58 has gotten that far, cam 60 makes contact with member 88 to close a circuit comprising a ground 98 through the cam and thence through contact 88, lead 90, battery 92, coil 94 and ground 96. When this circuit is closed, thereby energizing coil 94, the latter attracts the arm of switch 36 away from coil 74 and closes the circuit of which switch 36 is a part. Thereupon the complete indicating circuit is closed and the pointer registers. If at that time, the amount of iodine present as indicated by the ammeter reading is not more than the pre-set value indicated by contact member 40, the entire sequence of operations repeats itself until the iodine concentration as indicated by microammeter 32 is sufficient to drive the pointer away from contact 40.

Generally, the quantity of agent, for example iodine, that is generated in any given cycle is sufficient to move the pointer of the microammeter away from contact 40. If desired for any reason, however, a lesser quantity per cycle can be generated merely by adjusting the current value or time of generation or both. In such an event the ammeter can be provided with a contact indicating an upper pre-set limit of concentration. To make such a system operative automatically, the arrangement can be provided with a circuit extending from a ground through the upper contact then through a coil operatively associated with switch 50 and thence to a ground. Then when the concentration was at the upper level indicated by the second contact, its circuit would be activated automatically, opening switch 50 and thereby cutting off power to the cycle timer motor. When the concentration is not sufficient to operate that circuit, the cycle timer motor can be adjusted to providing continuous or repetitive cycles so that iodine can be generated until sufficient has been accumulated.

A typical schematic wiring diagram and cam system, operated from an A.C. source with internal rectification as needed, for a system in accordance with the invention is shown in FIG. 2. In operation, A.C. power from any suitable source (not shown) enters the system upon closing the main switch 102. That immediately puts current through leads 103 and 105 into the primary winding 104 of a transformer 106. The secondary coil 108 of the transformer 106 feeds into a conventional rectifier tube 110. The resulting D.C. current leaves the rectifier and enters the system through a lead 112, which is connected to a first electrode 114 in the titration vessel (not shown in FIG. 2). A center tap lead 116 to the secondary coil 108 of the transformer 106 completes the D.C. current inlet source. To minimize variations due to the A.C. source of current, an input filter comprising a pair of capacitors and a choke coil, all generally indicated by the numeral 118, can be placed across leads 112 and 116 in the usual manner.

Primary control of the system is effected by means of a current meter 120 having associated therewith a conventional meter relay. This indication circuit includes electrode 114, lead 112, a tap lead 122 from a voltage divider 124 and then into one side of a coil 126 in the relay meter. The other side of coil 126 is connected through potentiometer 128 to a lead 130 that extends to a second electrode 132 in the titometric vessel. When the concentration of the electrolysis product in the electrolyte falls below a pre-set value, current passing through

coil 126 is decreased thereby allowing the pointer 134 to touch contact 136 in the meter; in this manner, operation of the automatic correction mechanism is initiated as will now be explained.

The pointer 134 is connected to the current source through its lead 138 to inlet lead 112. The contact 136 of the meter 120 has a lead 140 through a relay coil 142 then to a contact 144 on a microswitch actuated by cam S_3. As will be explained hereinafter, the normal setting of cam S3 is such that the contact 144 is closed at the start of a cycle. Accordingly, the circuit is completed through lead 146 to a voltage divider 148 and then to a current source, lead 116.

With current flowing in relay coil 142, its associated switch 152 is closed, and A.C. power is placed across the cycle timer motor coil 160 by the following circuit: a lead 162 from A.C. inlet lead 103, through lead 164 to the motor coil 160, and then through a lead 166 tapped to a lead 170 through the contacts of switch 152 and then back to the A.C. source by electrical lead 172 to the second of the A.C. source leads 105. This initiates a cycle.

A shaft (not shown in FIG. 2) interconnects cams S_1, S_2, S_3, S_4 and S_5, which operate microswitches associated therewith. Accordingly, when the cycle motor starts, as just indicated, the cams influence their respective microswitches. The rotation of cam S_5 closes its operative contact 172 through switch arm 174, lead 176 to lead 172 and then to the A.C. power source. The other side of the switch is connected by a lead 178 to the lead 166 which goes through the motor coil 160, leads 164 and 162 and back to the other side 103 of the A.C. power source. This puts A.C. power across the motor for as long as cam S_5 keeps the switch closed. From the cam characteristics shown in FIGURE 3, it will be evident that cam S_5 closes its switch promptly after the cycle motor starts and keeps it closed until substantially the end of a cycle.

Referring again to FIGURE 3, it will be noted that cam S_4 has its spring member 180 against the upper open contact as the cycle starts. Shortly thereafter, it permits the spring 180 to close against contact 182, thereby closing a circuit comprising spring 18, contact 182, lead 184 and lead 186, these extending to a standard instrument counter 188. In this fashion, the number of cycles can be automatically recorded.

FIGURE 3 shows that at the start and end of a cycle, cam S_3 holds its spring 145 raised to close contact 144. Towards the end of the cycle, this cam closes the spring 145 against contact 192. This puts current through relay coil 193 via lead 194, through the relay coil, through lead 196 that is tapped to lead 138 and then to D.C. inlet lead 112. The other side of the circuit extends through lead 146 to the other D.C. inlet lead 116. With D.C. current in coil 193, switch 198 is closed thereby putting A.C. current in a reset coil circuit that extends from inlet lead 105, lead 172, lead 200, through switch 198, through lead 202 to the reset coil 204 in meter relay 120, and then through lead 164 back to the power source 103. The reset coil serves to move the pointer 134 away from contact 136 thereby opening the circuit of which contact 136 is a part and permitting the motor 160 to stop at the end of its cycle if the quantity of agent in the titrometric vessel is above the preset minimum. The opening of the pointer contact circuit de-energizes coil 142, releasing contact 152. However, current continues to flow to the motor through the by-pass line 172–176 around relay 142.

The initiation of the functions affected by a cycling of the timer motor and its microswitches is the determination that an inadequate quantity of the desired agent is in the titrometric vessel. A major one of these functions is to generate additional quantities of this agent. This is controlled by cam S_2 which, as is shown in FIG. 3, closes its operative circuit shortly after the cycle timer motor is locked-on through cam S_5. The generation circuit operated by cam S_2 comprises the spring contact 210, microswitch contact 212, lead 214 to voltage divider 216, and then to lead 116 to the power source and then through lead 112 to electrode 114. The other side of the circuit extends from the spring 210 through lead 220 to the third electrode 222.

The remaining cam S_1 is provided to send an A.C. current to a stepping relay differentiation circuit to record the cycling rate as a function of time. Such circuit is not shown, for though it is useful, it is not essential to operation of the analyzer.

It will be noted from the foregoing description of the specific embodiments of FIGURES 1 and 2 that electrolytic generation of the agent that reacts with the material to be indicated occurs only when use of the indication circuit is not needed. Hence, the current used for electrolysis does not interfere with the indication circuit and the sensitivity and accuracy of that circuit is correspondingly enhanced. This is of particular importance, especially in view of the fact that monitoring is affected through detection of the electrolysis product and recordation of the quantity thereof used.

The analyzer of this invention is of primary importance for monitoring atmospheres for boranes. In view of the established maximum allowable concentrations (MAC) of the boranes, it is evident that a monitor has to be particularly sensitive to be acceptable. Use of the present monitor, with potassium iodide as the precursor for the generated electrolysis product, has been shown to be adequately sensitive. The electrolysis product, iodine, has a reaction stoichiometry with various boranes that is very favorable. The following are data calculated from reaction stoichiometry of various boranes with iodine:

Table I

	Meq. reducing power per mm. for I_2 Oxid.	Eq. wt.	Microequivalents per 1 liter air (20° C./1 atm.)	MAC conc., mmg./m.[3]
B_2H_6	6	4.62	0.022	100
B_4H_{10}	20	2.67	[1] 0.037	[1] 100
B_5H_9	20	3.16	[1] 0.032	[1] 100
$B_{10}H_{14}$	40	3.06	0.098	300
$B_{10}H_{14}$	40	3.06	[1] 0.033	[1] 100

[1] Assuming 100 micrograms per cubic meter of air is maximum allowable concentration.

From these data it is evident that to provide appropriate warning that the borane concentration is dangerously approaching the MAC, a borane monitor operating on the basis of an iodine titration will have to produce and easily detect amounts of iodine in the 0.02 microequivalent range. As data presented hereinafter shown, the present invention readily meets this rigid standard. An example of a test of this sensitivity is as follows: Two platinum foil electrodes, 1 cm. by 2 cm. and 1 cm. by 1 cm. in area, with an impressed potential of 0.02 volt D.C. gave a signal of 25 microamps when 2 microequivalents of iodine were added to 100 ml. of a potassium iodide solution buffered at pH 5.5 with a pyridine-pyridinium buffer. The addition of 1.2 microequivalents of pyridine borane to that solution reversed the indication current by about 20 microamps.

In order to test the operation of a device in accordance with the present invention, both batchwise and continuous titrations were run. A cell electrolyte was prepared by dissolving two grams of potassium iodide in 500 milliliters (ml.) of 0.5 M sodium bicarbonate. The cell was filled with 100 ml. of this buffered electrolyte. To operate the instrument, the meter relay contact (FIG. 2) was set and the main switch turned on. The titrator immediately started to cycle and generated iodine. When enough iodine was present to yield an amperimetric signal greater than the set signal, the titrator stopped cycling. Then

samples of boranes, as hereinafter described, were added to the titration cell; for batch titrations, the samples were added from a pipet while those for continuous titrations were added from a buret. Gas samples were tested by pumping prepared samples through the titration vessel.

Snythetic gas samples were prepared by passing dry nitrogen over a volatile boron hydride in a different apparatus (Anal. Chem. 29, 123 [1957]). In making diborane gas samples, the diborane was first dissolved in mineral oil and then the dry nitrogen was passed over it. Decarborane was used as such in the diffusion apparatus. Routine sampling indicated that gas samples of constant composition were obtained.

In the batchwise coulometric titrations, various amounts of 0.001 N pyridine-borane were run by pipetting samples directly into the cell. For this operation, the circuit characteristics were set to provide a generation current of 10.21 milliamps and the meter relay (indication circuit) was set to switch, or start a generation cycle, at a current of 20 mircoamps. Results of the titrations are given in the following table. The calculated results were based upon titration of the pyridine-borane stock sample with standard iodine.

Table II

Sample No.	Sample Vol. (ml.)	Sample Cycles	Microequivalents Present [a]	Microequivalents Found	Percent Differences
1	8	34	14.8	14.4	−2.7
2	10	44	18.5	18.6	+0.5
3	10	45	18.5	19.1	+3.2
4	14	62	26.0	26.3	+1.2
5	20	87	37.0	36.9	−0.3
6	20	84	37.0	35.6	−3.8
7[b]	24	104	44.4	44.0	−0.9
8[b]	18	78	33.3	33.0	−0.9
9[b]	13.40	61	24.8	25.8	+4.8
10[b]	12.07	56	22.4	23.7	+5.8
Average Percent Difference					+0.61±3.0 Sd

[a] Calculations made on basis of iodometric titration of stock solution of pyridine-borane.
[b] Sample added dropwise from a buret.

In runs 7 through 10 of Table II, the samples were added dropwise from a buret. The titrator followed the buret flow within one or two cycles. In other examples, samples of decarborane in hexane were titrated batchwise in the analyzer using a generation current of 300 microamps. The titration medium was the potassium iodide electrolyte containing the bicarbonate buffer. The results obtained in a series of these runs are:

Table III

MICROEQUIVALENTS $B_{10}H_{14}$

Sample No.	Present [a]	Found	Cycles	Percent Differences
1	0.538	0.560	45	+4.2
2	0.538	0.573	46	+6.5
3	0.538	0.523	42	−2.8
4	0.538	0.573	46	+6.5
5	1.076	0.970	78	−9.7
Average Percent Difference				+0.9±7.1 Sd

[a] 40 meq. per millimole.

An air stream containing decarborane was also tested in the analyzer with the bicarbonate buffered electrolyte. Simultaneously, the air stream was analyzed by a colorimetric method known to be quite accurate. The data from these tests are as follows:

Table IV

DETERMINATION OF DECABORANE IN AIR P.P.M. OF $B_{10}H_{14}$ BY VOLUME

Run No.	Borane Monitor	Colorimetric Method
1	0.29	10.25
2	0.24	0.29
3	0.26	0.30
4	0.15	0.16

[1] Known loss in colorimetric method.

The results shown in Table IV are considered to show excellent agreement between the two systems, especially considering the low concentration of decarborane that was involved.

As the discussion above shows, the invention is characterized by titration in which the titration agent is generated periodically as discrete quantities of agent. This manner of operation can be readily applied to the detection and monitoring of substances other than boranes. For example, in the following table are data obtained in using these devices with a 300 microamp generation current for the detection of small amounts of arsenous oxide.

Table V

COULOMETRIC TITRATION OF PRIMARY STANDARD ARSENOUS OXIDE

Sample No.	As_2O_3 present [1]	As_2O_3 found [1]	Cycles	Percent Diff.
1	0.141	0.137	11	−2.8
2	0.617	0.622	50	+0.8
3	0.617	0.646	52	+4.7
4	0.617	0.597	48	−3.2
5	0.617	0.646	52	+4.7
6	0.617	0.671	54	+8.8
Average Percent Difference				+2.16±4.6 Sd

[1] Micro-equivalents.

The excellent agreement of the actual quantity of the oxide present with that determined by the analyzer is evident in these data.

From the foregoing discussion and data, it is evident that the automatic continuous coulometric titrator that constitutes the present invention is capable of determining boranes and other materials in concentrations near the maximum allowable concentration. Since the maximum allowable concentration for all boranes is very low, the fact that the monitor does not differentiate from among the boranes is immaterial, any borane concentration indication by the monitor being significant. Moreover, in view of the high sensitivity of the device, only reasonably sized samples of the atmosphere need be used.

The system described is particularly advantageous in that interference by collateral materials is negligible. Only those materials which react with iodine, such as acetone or peroxides or the like, seem to interfere. In tests with this monitor of laboratory and plant air, the monitor readily detected boranes in one laboratory in which volatile borane-containing samples were being analyzed. The boranes were detected only when the borane samples were exposed to the laboratory air.

Other characteristics of the invention that contribute to the accuracy and sensitivity of the device are apparent upon considering the foregoing discussion of the apparatus. The values of the generation current and the indication current can be accurately set and maintained by simply varying the circuit resistances. Once having established the generation current, the quantity of electrolysis product produced in each cycle is steady since the cam characteristics and motor speed are very constant quantities.

In accordance with the provisions of the patent statutes, the invention has been described and illustrated with what is now considered to be its best embodiment. However,

it should be understood that, within the scope of the appended claims, the invention can be practiced otherwise than as specifically illustrated and described.

We claim:

1. A continuous automatic coulometric titration system comprising, in combination with a titrometric vessel containing an electrolyte, means responsive to the concentration of a titrometric agent in said electrolyte in said vessel, sensing means operatively associated with said titrometric vessel indicating when the concentration of said agent therein falls below a predetermined value, means automatically responsive to said indication by said sensing means to impress a predetermined constant D.C. current across said electrolyte for a predetermined fixed period of time, whereby a predetermined fixed quantity of titrometric agent is generated, means operative upon each said generation of titrometric agent indicating the number of times said agent is generated, and means to deliver samples of the material to be monitored to said electrolyte in said vessel.

2. A method for the quantitative analysis of boranes by titration, comprising absorbing boranes in an electrolyte, electrolytically generating a fixed incremental quantity of titrating agent in said electrolyte, periodically electrolytically determining the quantity of said titrating agent in said electrolyte and electrolytically generating an additional quantity of said agent essentially equal in amount to said first mentioned quantity each time the quantity of said agent in said electrolyte falls below a predetermined value, the number of times said agent is generated indicating the total quantity of said titration agent produced and then consumed in titrating said boranes.

3. A method in accordance with claim 2, in which said electrolyte contains potassium iodide and said titrating agent is iodine.

4. A continuous automatic coulometric titration system comprising a vessel containing an electrolyte, said electrolyte containing a substance that upon electrolysis results in a material in said electrolyte in a quantity proportional to the product of the electrolysis current and the time of flow of electrolysis current, a first constant flow direct current power circuit comprising first and second electrodes in said electrolyte, a D.C. power source and a current indicating means, a second constant flow direct current power circuit comprising a D.C. power source, a pair of electrodes in said electrolyte and a switch, a third circuit comprising an A.C. power source, an electric motor and a switch responsive to said indicating means in said first direct current circuit, a fourth circuit comprising a power source, a switch and a counting means, a fifth circuit comprising an A.C. power source, a switch and said electric motor, at least four mechanical means operative by said motor, a first of said mechanical means associated with and operative to close said switch in said circuit including said A.C. power source and said motor for a predetermined time, said second mechanical means operative to disengage said switch that is responsive to said indicating means after said first mechanical means closes the switch associated therewith, said third mechanical means associated with and operative to close said switch in said circuit including said counting means for a period of time just sufficient to count once for each cycle of said first mechanical means, and said fourth mechanical means operative to close said switch in said second direct current circuit for a fixed period of time that commences after said first mechanical means closes its circuit and ends before said first mechanical means permits its circuit to open whereby electrolysis in said electrolyte occurs for a fixed time during each cycle of said first mechanical means.

5. A continuous automatic coulometric titration system comprising a vessel containing an electrolyte, first, second and third electrodes in said vessel extending into said electrolyte, said electrolyte containing a substance that upon electrolysis results in a material in said electrolyte in a quantity proportional to the product of the electrolysis current and the time of flow of said current, a first constant flow direct current power circuit including said first and second electrodes, current indicating means in said first direct current power circuit, a second constant flow direct current power circuit, said second circuit including said third electrode and one of said first and second electrodes, an electric motor, a separate power source for said motor, at least three switches associated with said motor, a circuit including one of said switches and a counting means, an A.C. circuit including a second of said switches and said motor, said third switch being in said second constant flow direct current circuit, means operatively associated with said current indicating means and including an A.C. power source responsive to a predetermined set value indicated by said current indicating means to start said motor, first mechanical means operating on the second of said switches and operative by said motor to maintain closed said second of said switches for a predetermined period of time, whereby A.C. power is supplied to said motor for that period of time, second mechanical means operating on the first of said switches and operative by said motor to operate said switch in said circuit including said counting means to count once each cycle of said motor, and third mechanical means operative by said motor to close and maintain closed said switch in said second constant flow direct current circuit for a fixed period of time extending within the limits of time that said second switch closes said A.C. circuit to said motor.

References Cited in the file of this patent

UNITED STATES PATENTS

2,832,734	Eckfeldt	Apr. 29, 1958
2,928,782	Leisey	Mar. 15, 1960

OTHER REFERENCES

De Ford et al.: Analytical Chemistry, volume 23, July 1951, pages 938–944.

Sease et al.: Analytical Chemistry, volume 19, 1947, pages 197–199.

Ephraim: "Inorganic Chemistry," 1948, page 788.

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,162,585 December 22, 1964

Donald D. De Ford et al.

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

Column 5, line 43, for "spring 18" read -- spring 180 --; column 6, line 58, for "0.02" read -- 0.2 --; column 7, line 11, for "Decarborane" read -- Decaborane --; lines 49 and 71, for "decarborane", each occurrence, read -- decaborane --; same column 7, Table II, under the heading "Percent Differences", line 9 thereof, for "4.8" read -- 4.0 --; column 8, Table IV, under the heading "Colorimetric Method", line 1 thereof, for "10.25" read -- 0.25[1] --.

Signed and sealed this 4th day of May 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
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