Oct. 24, 1944. O. KANNER ET AL 2,361,295

METHOD AND APPARATUS FOR MAKING CHEMICAL ANALYSES

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Fig. 1

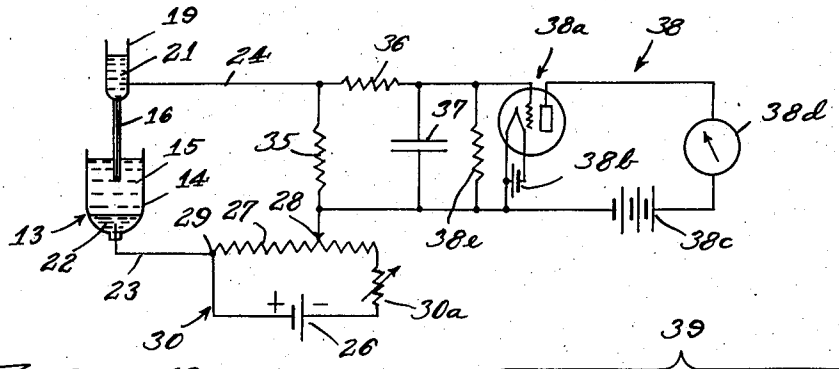


Fig. 2

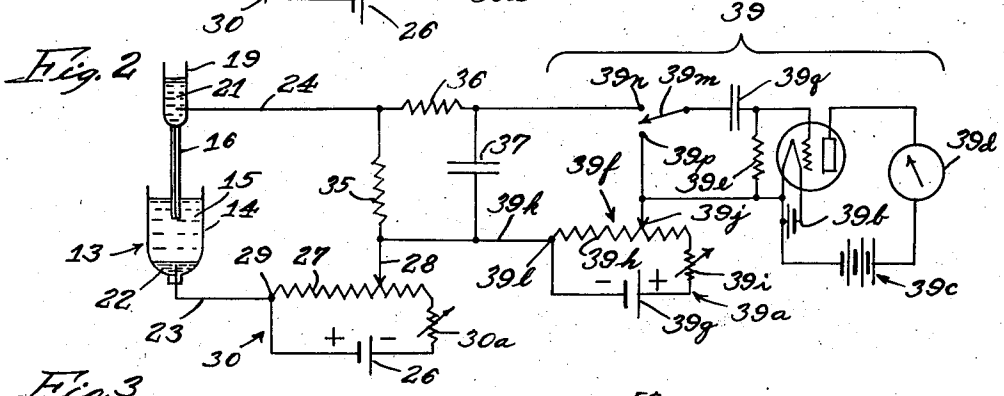
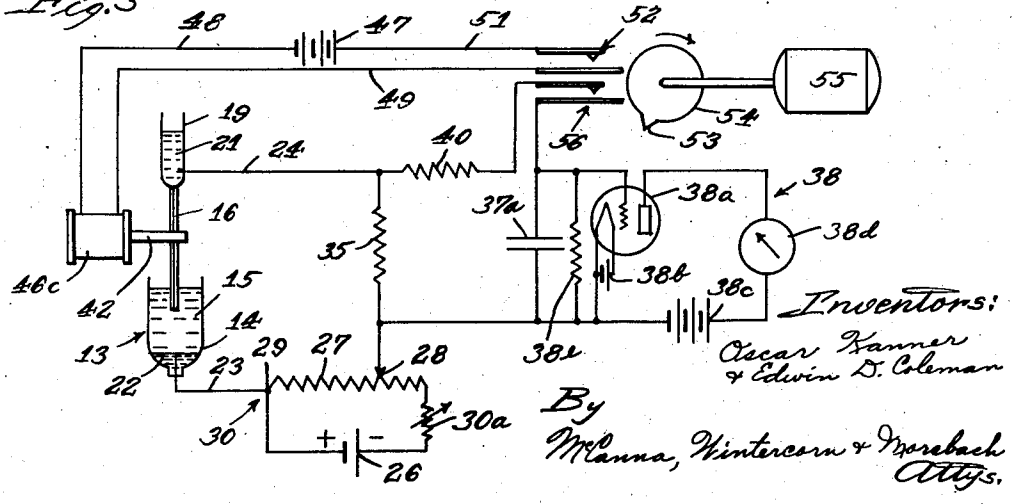


Fig. 3



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Fig. 4

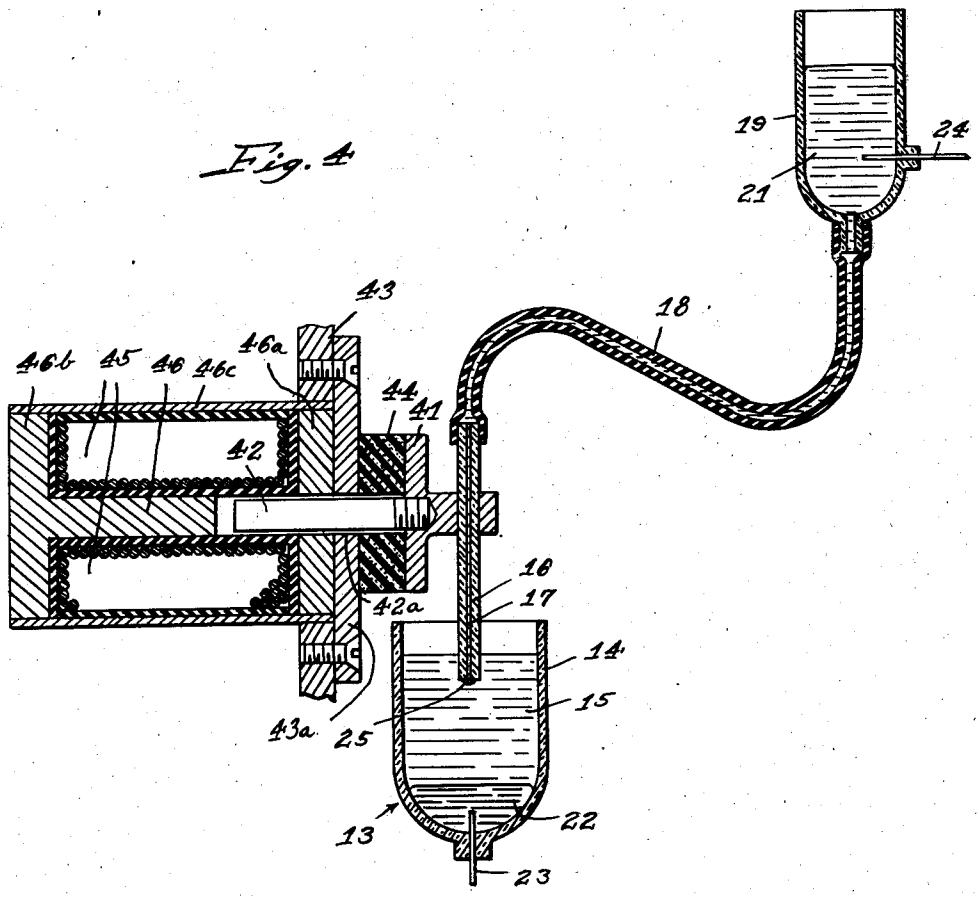
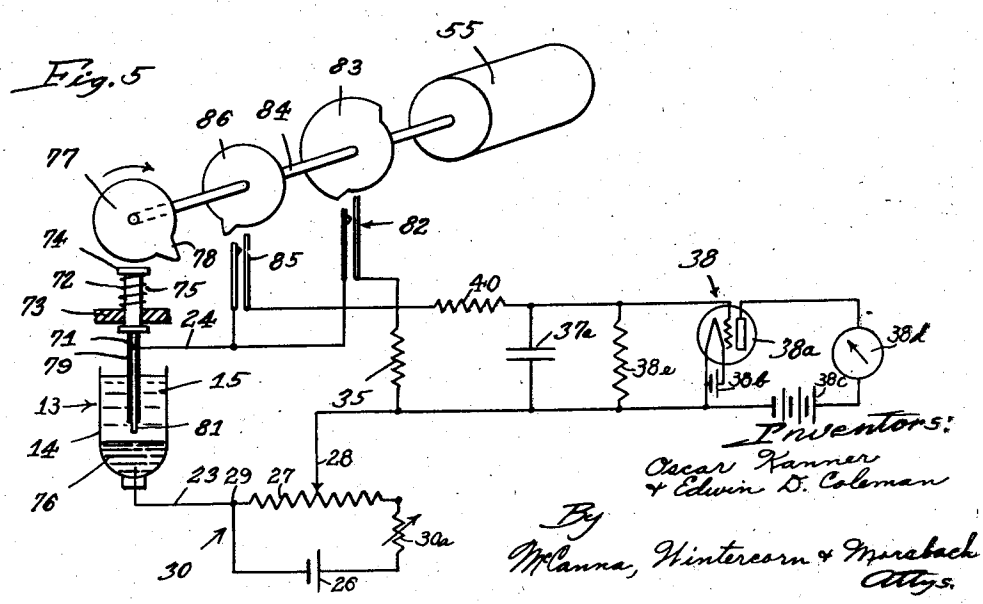


Fig. 5



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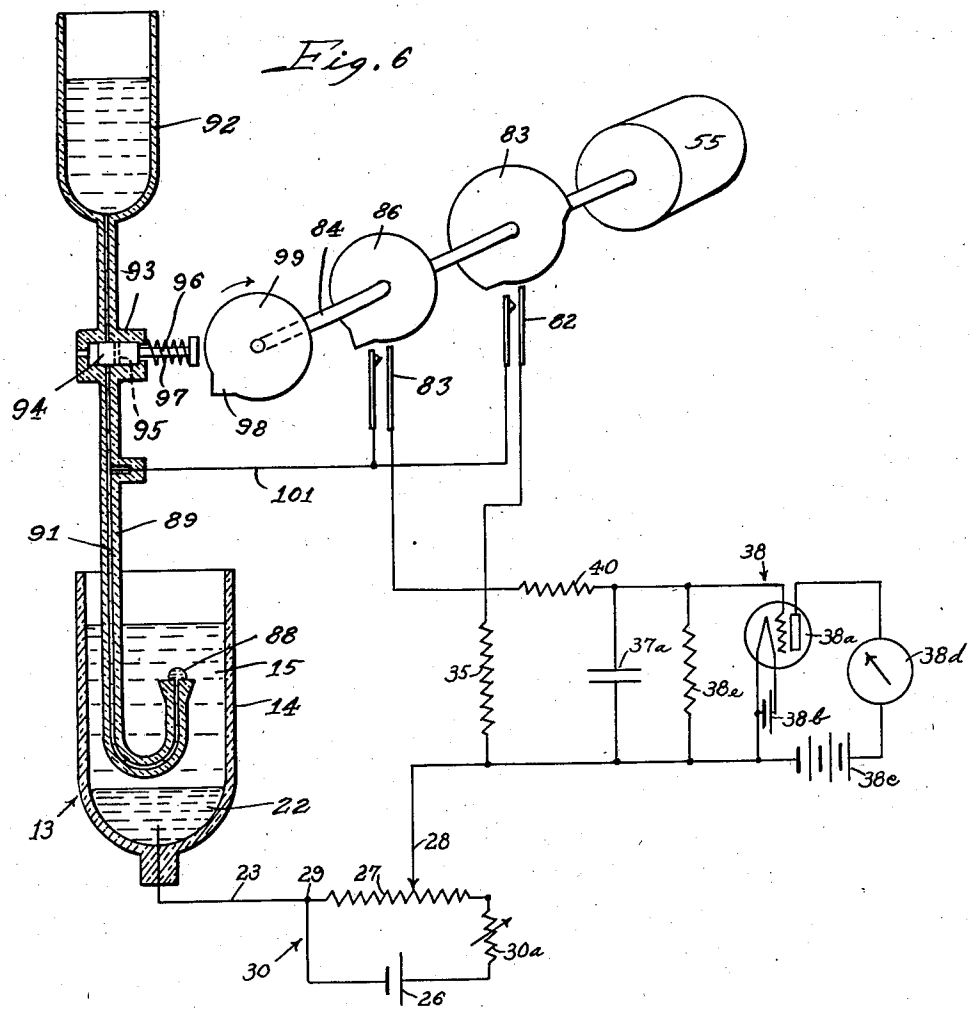
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METHOD AND APPARATUS FOR MAKING CHEMICAL ANALYSES

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Fig. 6



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UNITED STATES PATENT OFFICE

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METHOD AND APPARATUS FOR MAKING CHEMICAL ANALYSES

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Application January 6, 1941, Serial No. 373,326

29 Claims. (Cl. 175—183)

This invention relates to improvements in the method and apparatus for making chemical analyses of the broad class in which an electric current is passed between a test and a reference electrode immersed in the liquid under test, the voltage applied to the electrodes being progressively varied and the current being measured. The corresponding currents and voltages are plotted to form a curve from which the desired chemical data are obtained. This type of chemical analysis is well known in the literature and has been described by Heyrovsky and Kolthoff, and the method has variously been known as "polarographic" method of analysis, "voltametric" determination and "amperometric" titration. The invention is herein described with special application to the so-called dropping mercury electrode, but certain phases of the invention are not limited to this particular type of electrode and are of merit regardless of whether the test electrode is stationary or moving, liquid or solid, though the preferred embodiment of the invention contemplates a dropping mercury electrode, and the invention has particular merit in conjunction therewith.

The dropping mercury electrode is now well known in the art, and the theory thereof has been discussed in considerable detail in the scientific literature, particularly in the writings of Heyrovsky and Kolthoff. Basically the dropping mercury electrode comprises a glass tube having a very fine capillary through which mercury is flowed, ordinarily under hydrostatic pressure. The diameter and the length of the capillary are such that the mercury is delivered from the open end at a rate of the order of one drop each three seconds. The delivery end of the tube is immersed in the liquid under examination, and the forming drops of mercury (which form one by one) are the test electrode of a cell. Such electrodes are commonly known as dropping mercury electrodes although other fluid metals may be used therein, such, for example, as gallium which is fluid at slightly elevated temperatures, and the term "dropping mercury electrode" as herein used contemplates an electrode of this type regardless of the specific nature of the fluid metal employed. The electrolyte is the fluid under examination, and the reference electrode is usually a non-polarizable electrode in electrical connection with the fluid under examination, frequently being a pool of the mercury rejected from the capillary. The non-polarizable electrode may be a material other than the mercury pool, as above mentioned. Electrical connection is established to the forming mercury drops by way of the column of mercury in the capillary and the mercury in the reservoir from which the capillary is supplied. Voltage is applied to the cell thus formed from a battery or other suitable source of electromotive force and the current flowing through the cell is measured by a galvanometer.

It has been found that if an electrical potential, beginning at zero and gradually increasing in magnitude is applied to such a cell, the current flowing through the cell does not increase uniformly in accordance with Ohm's law. Instead, the first small increment of potential applied to the cell results in substantially no flow of current therethrough and substantially no current flows with increase of potential until the applied potential becomes sufficiently high to force the deposition of that substance in the liquid under examination which is most easily deposited at the test electrode. When the potential applied to the cell reaches this value, current begins to flow by virtue of the deposition of said substance at the test electrode. Other things being equal, the magnitude of this current is proportional to the concentration of said substance, so that the current increment occurring at this potential value is a measure of the concentration of said substance and is therefore a basis for the quantitative determination thereof. Furthermore, the potential value necessary to cause the deposition of said substance is indicative of its identity, and thus serves as a basis for the identification thereof. If the potential applied to the cell is now further increased, no corresponding increase in the cell current is produced until the impressed potential reaches a value necessary for the deposition of the next most easily deposited species, whereupon there again appears a sharp increase in the flow of current, the magnitude thereof depending upon the concentration of the second mentioned species. Here again the magnitude of the current increase is a measure of the species concentration, and the potential value a key to its identity. This phenomenon may be repeated with several additional species as the potential is successively increased, until finally a potential is attained at which some highly concentrated species is forced to deposit and beyond which potential the relationship just outlined is lost and the cell begins to obey Ohm's law.

As implied above, the magnitude and the potential value of these current steps are the basis of a system of chemical analysis. In one appa-

ratus now known in the art and called a "polarograph," means are provided for automatically producing a chart or recording showing the current-voltage relationship, the device including means whereby the potential is continuously increased and concurrent readings of the galvanometer recorded. In so-called "amperometric" titrations, a simple potentiometer and galvanometer are commonly used, the potentiometer being set manually and the galvanometer readings being taken in the same manner, the two being plotted into a curve for the purpose indicated.

While the flow of current through such a cell depends on the concentration of the substance being deposited, it depends also on the rate at which mercury flows through the capillary and varies also with the area of mercury exposed to the solution, or in other words, with the size of the mercury drop. It is therefore obvious that the flow of current changes constantly during the life of each mercury drop. As a result, the galvanometer of such a circuit must continuously oscillate in an attempt to follow the alteration in the current as successive drops form and fall, and therefore its readings are far from constant. When the data are recorded with a device such as the "polarograph" this variation appears as a very marked waver in the current voltage curve, which seriously interfere with precise readings of the data and therefore result in considerably less analytical accuracy than might otherwise be obtained. Attempts have been made to minimize this difficulty by utilizing a galvanometer with a rather long natural period, and by using a comparatively high dropping rate from the capillary, but it has been found that under conditions prevailing with such instruments dropping rates much greater than thirty per minute are unsuitable and that a rate of twenty per minute is a more satisfactory rate, the galvanometer being designed with a long natural period and then critically damped. With this arrangement readings are rather slowly obtained and are of limited precison.

An important object of the invention is the provision of a generally improved method and apparatus for making chemical determinations of the class described, wherein objectionable features inherent in prior art devices are eliminated.

Another object of the invention is the provision of a device of the character described wherein the current values on the current-voltage curve are determined by measuring the potential across a resistance in the circuit of the cell.

A still further object of the invention is the provision of a device of the character described in which the current flowing through the cell is measured at a predetermined phase in the life of each mercury drop.

A further object of the invention is the provision in a device of the character described of novel forms of electrode carriers, and of novel means for operating the same.

A still further object of the invention is the provision of a device of the character described having a dropping mercury electrode wherein means are provided for starting a new drop at the end of the capillary and for measuring the current at a predetermined time after the starting of the drop, whereby the current measurement on each drop will be made when the drops are of uniform size and age.

Another object of the invention is the provision of a method of the character described wherein the current to a drop is sampled at the same instant in the life of each drop and is caused to give a continuous response.

Another object of the invention is the provision of means for causing the release of the drop from the capillary tube promptly after the sampling of the current.

A still further object of the invention is the provision of mechanical means for discarding the mercury drop promptly after it has served its purpose.

Other objects and advantages will appear from the following description and the accompanying drawings, in which—

Figure 1 shows an embodiment of one phase of the invention wherein the values of the current-voltage curve are determined in response to the IR drop across a resistance in the cell circuit by a high impedance measuring device of large time constant;

Fig. 2 is a device similar to that shown in Figure 1 employing a potentiometer and a thermionic tube circuit as a null indicator;

Fig. 3 shows a further embodiment of the invention wherein means are provided for sampling the current to the mercury drops at exactly the same instant in the life thereof and for causing the current to produce a continuous response;

Fig. 4 is a view partly in section showing the capillary tube and mechanical means for disposing of the drops after they have served their purpose;

Fig. 5 is a diagrammatic view showing a modified form of electrode and electrode carrier, and

Fig. 6 is a diagrammatic view showing a still further form of the invention.

Referring first to Figure 1, the device therein shown includes a cell indicated generally by the numeral **13** and shown more in detail in Fig. 4, this being the conventional form of dropping mercury electrode cell and including a vessel **14** in which the sample under test is positioned as indicated at **15**. Suspended above the sample **15** with its lower end submerged is a capillary tube **16** forming the electrode carrier and having a capillary **17**. In this instance a rubber tube **18** connects the opposite end of the tube to a reservoir **19** containing mercury as indicated at **21**. We have herein shown for purpose of illustration a mercury pool **22** positioned in the bottom of the vessel **14** and serving as the reference electrode of the cell, though, as previously described, in special circumstances other types of reference electrodes will be used as is well known in the art. The mercury pool is generally covered with calomel to assist depolarization and a low concentration of a soluble chloride, such as potassium chloride or lithium chloride may be dissolved in the liquid under test. Means are provided such as a conductor **23** for making electrical contact with the mercury pool **22**, and likewise a conductor **24** serves to make electrical contact with the mercury in the reservoir **19**. The reservoir **19** is commonly disposed at an elevation above the capillary tube so that the mercury will flow through the tube and form at the end thereof in the form of small drops as indicated at **25**. Conveniently the capillary is of such size that the drops will normally form and fall at the rate of about one drop each three seconds. It will be understood that the actual diameter and length of this capillary may vary, depending upon the elevation of the reservoir and other factors. Where special means are provided for disposing of the drop, the dropping rate may be

varied through a wide range, as will presently be described.

A battery **26** is connected in series with a reasonably low resistance **27**, for example, up to about three hundred ohms, which is provided with a sliding connection **28** by means of which suitable voltages may be produced between the point **28** and a point **29**. This is the usual calibrated potentiometric circuit and includes the battery **26** suitably of about four volts and a variable resistance **30***a*, the circuit hereafter being referred to by the numeral **30**. The conductor **23** to the reference electrode is connected to the point **29**. The conductor **24** from the mercury reservoir is connected to the slider **28** through a resistance **35** suitably between about two thousand and one hundred thousand ohms depending upon the composition of test sample. A resistance **36** is connected in series with a condenser **37** across the resistance **35**, the values of resistance **36** and condenser **37** being sufficiently large so that the variations in potential over the condenser **37** with rate of change of current through the resistance **35** (during the individual drop life) can be ignored or offers no serious difficulty to reading. A vacuum tube voltmeter designated generally by the numeral **38** is connected across condenser **37** and is scaled to indicate the current flowing in the resistance **35**. Since such a vacuum tube voltmeter draws very little current it is possible to use relatively small values for the resistance **36** and condenser **37**, and we have found that a resistance of ten megohms at **36** and a capacity of one microfarad at **37** is a suitable combination, although it will be recognized that the most convenient time constant will depend upon the performance characteristics desired. The vacuum tube voltmeter **38** may suitably comprise a type **30** vacuum tube **38***a*, a cathode exciting battery **38***b* of two volts, a plate battery **38***c* of about twenty-two and one-half volts, a plate meter **38***d* of about 0–5 m. a. sensitivity, and a grid leak **38***e* of about 50 megohms resistance.

In Fig. 2 we have shown a construction identical with that of Figure 1 with the exception that the vacuum tube voltmeter **38** is replaced by a potentiometric measuring device indicated generally by the numeral **39** comprising a vacuum tube voltmeter similar to that of Figure 1 having elements **39***a* to **39***e* similar in structure and function to elements **38***a* to **38***e* of Figure 1. A calibrated potentiometer **39***f*, comprising a battery **39***g* suitably of three volts, a variable resistance **39***h*, suitably of **250** ohms, and a uniform resistance **39***i* suitably of **250** ohms, and a sliding contact **39***j*, is connected by a conductor **39***k* from a connection **39***l* to one side of the condenser **37**. By moving the slider **39***j* there can be developed between the slider and the point **39***l* a potential equal and opposite to that produced in the condenser **37** by the current flowing through the test cell, and this condition of balance is determined by moving a switch element **39***m* between closing positions with respect to contacts **39***n* and **39***p*. When the balance is perfected, moving the switch between these two contacts produces no change in the charge on a condenser **39***q*, and consequently no change in potential of the grid of vacuum tube **39***a* of the vacuum tube voltmeter and no response in the meter **39***d* mounted in the plate circuit of the tube. Thus, the current flow through the resistance **35** is measured by adjusting the slider **39***j* or the uniform resistance **39***i* until the meter **39***d* shows no appreciable movement when the switch element **39***m* is moved between contacts **39***n* and **39***p*. This potentiometric circuit, we have found, gives more precise and accurate data than either the galvanometer or the vacuum tube voltmeter heretofore described.

It will be seen that with the forms heretofore described we have provided a quick and precise means for measuring the average potential existing over the resistance **35** which in turn gives the average current, and this value is quite as indicative of the concentration of the substance species as can be had by averaging galvanometer readings or by attempting to find the average value of a wavering trace line of a device such as the "polarograph." Furthermore, it permits of more rapid and more accurate determination.

While the constructions shown in Figs. 1 and 2 give more accurate results than prior art constructions and represent a distinct and substantial improvement thereover, they still are objectionable in that the method is slow and time-consuming. We have therefore devised an improved method and apparatus for still further increasing the speed and precision of the readings. As previously mentioned, with the instruments and methods of the prior art, difficulty is encountered when the dropping rate for the mercury drops is increased beyond about thirty drops per minute, since the determinations tend to become less exact when this rate is exceeded. This has been attributed to excessive stirring of solution at the higher dropping rates. We have found, however, that the dropping rate can be increased many times and simultaneously much greater precision obtained. For example, we have succeeded in using a dropping rate greater than two hundred and fifty and up to five hundred drops per minute and yet obtained materially greater accuracy than that known in the past.

In previous instruments of this nature the current through the cell is measured continuously and throughout the entire life of the drop, the average current being taken as indicative. According to our method, the current is measured at a predetermined phase in the age of the drop, that is, during a definite time increment beginning at a definite time interval after the drop has commenced to form. This we have found to be capable of producing highly improved results.

Referring now more particularly to Figs. 3 and 4, the form therein shown embodies the cell designated by the numerals **13** to **25** inclusive, the potentiometer **30**, and the resistance **35**. A holding circuit including a resistance **40**, a condenser **37***a* and a switch **56**, is employed to charge the condenser **37***a* at a particular instant in the life of a drop. In this circuit the charge on the condenser **37***a* is measured by a vacuum tube voltmeter identical with that shown at **38** in Figure 1 though other means of measurement are also suitable. Attached to the capillary tube **16** is a device adapted to be periodically energized for the purpose of disposing of the mercury drop at the end of the capillary tube. A suitable form of this device is best shown in Fig. 4 and includes a fixture **41** within which the capillary tube **16** is fixedly mounted. This fixture carries a soft iron core **42** which projects through an opening **42***a* in a collar **43***a* attached to the face of a mounting plate **43**. The fixture **41** is attached to a mounting member **44** of soft sponge rubber or similar material which is in turn fixed to the face of the collar **43***a*. On the opposite side of the plate **43** is mounted a solenoid having the conventional

windings 45, soft iron core 46, soft iron end members 46a and 46b and soft iron shell 46c which serve with the armature 42 to complete the magnetic circuit. It will be seen that when the coil 45 is energized, the armature 42 is suddenly drawn toward the core 46 thereby imparting an impulse to the capillary tube 16. The coil 45 is connected to a suitable energizing battery 47 by way of conductors 48, 49 and 51 and a normally open switch 52. The switch 52 is momentarily closed at periodic intervals by a cam 53 on a cam disk 54 driven at a constant speed, for example, from an electric motor 55 preferably though not necessarily a synchronous motor. When the switch 52 is closed momentarily, the magnet is energized, drawing the armature 42 inward and releasing the same so as to impart a sharp oscillation to the capillary tube. This causes the release from the end of the tube of the droplet of mercury which previously formed thereat. We have found that, if the spontaneous dropping rate is regulated to about five drops per minute or more, it is practical with the procedure herein disclosed to accelerate the dropping rate to a value as high as five hundred per minute and simultaneously to obtain satisfactory synchronism of the drops with the remainder of the mechanism presently to be described. It will be seen that this device acts to cause the drops of mercury to form as a series of closely and uniformly spaced incidents in a time frame.

While we have disclosed an electromagnet for imparting a mechanical shock or impulse to the capillary, it will be apparent that similar results can be obtained by mechanical means such as a mechanical knocker or linkage actuated by the cam 53 or otherwise, and the invention is not to be construed as limited to the particular apparatus disclosed.

Interposed in the circuit between the resistance 40 and condenser 37a is the normally open switch 56 positioned to be actuated by the cam 53 just prior to actuation of the switch 52 so that after actuation of the switch 52 the cam advances through almost a complete revolution before actuating the switch 56. It will be seen that during this period of time, current has been flowing in the cell circuit from the potentiometer 30 through the forming drop, the conductor 24 and the resistance 35, this current increasing in magnitude with size of the drop surface. The cam 53 then engages the switch 56 momentarily closing the same and impressing on the condenser 37a a potential dependent on the IR drop in resistance 35, which in turn is dependent on the nature of the solution under examination and upon the life of the drop as well as on the potential impressed on the circuit by the potentiometer 30. The switch 56 then immediately opens so that the charge impressed on the condenser 37a cannot be altered by subsequent changes in the current through the resistance 35. The resistance 40 which is placed in series with the resistance 35 and the condenser 37a functions to smooth out minor errors due to imperfect contact action or imperfect timing. After closing and opening the switch 56, the cam 53 advances a minimum practical distance and then momentarily closes switch 52 to cause release of the drop from the capillary tube and engender the birth of a new drop. The charge on the condenser 37a is measured by the vacuum tube voltmeter 38 as heretofore described. The speed of the cam 53 is such as to cause prompt response of the meter 38d to the drop in resistance 35 so that, when the potential impressed on the cell from 30 is altered, the current flowing in the cell circuit is at once apparent to the operator from the position of the meter. We desire to point out that the vacuum tube voltmeter 38 of Fig. 3 may be replaced by the potentiometric measuring device 39 of Fig. 2, and as previously stated, this will produce somewhat more accurate results. A quadrant galvanometer or other voltage measuring device of high input resistance may also be satisfactorily used.

In Fig. 5 we have shown a further embodiment of the invention employing what is herein termed a "dipping mercury electrode." This type of electrode includes an electrode carrier 71 which preferably may consist of amalgamated gold, platinum or other similar inert metal. This electrode carrier is supported for longitudinal movement by any suitable means, as, for example, by a cylindrical plunger 72 supported in a guide member 73, the plunger having an enlarged head as shown at 74 against which a spring 75 acts to urge the plunger to its elevated position. A pool of mercury designated generally by the numeral 76 is disposed in the test vessel 14 below the test solution 15 in such position that when the electrode carrier is moved downwardly it dips into the mercury to coat all the amalgamated metallic surface thereof. The electrode is moved to its lower position by a cam disk 77 carrying a cam surface 78 adapted to engage the end of the plunger 72 to urge the electrode down against the action of the spring 75. It will be understood that the electrode carrier is insulated from the plunger 72 and associated parts and is enclosed in its upper portions in an insulating sheath 79 which exposes only the lower portion of the metallic electrode carrier 71. During the cycle the cam 78 depresses the electrode carrier until the exposed metallic portion indicated by the numeral 81 is completely beneath the surface of the mercury 76. Thereafter the spring 75 acts to elevate the carrier until the surface 81 is completely separated from the mercury but is still completely immersed in the liquid 15. It will be seen that each time immersion of the electrode carrier is effected, the old mercury surface is removed and a fresh mercury surface is produced on the exposed portion 81. After the electrode is lifted by the spring 75 and comes to rest, a short period of time is allowed to elapse and the cell formed by the mercury pool, the test liquid and the freshly amalgamed surface 81 has potential applied thereto in the manner heretofore described by connecting the potentiometer 30 in circuit therewith through the conductors 23 and 24, the resistance 35 and a switch 82, a cam 83 disposed on a shaft 84 of the motor 55, which shaft also carries the cam disk 77, acting to close the switch 82. Current then begins to flow through the electrode surface, and this initiates the time cycle, since it will be seen that the closing of the switch 82 in principle corresponds to the start of the formation of a mercury droplet discussed in connection with Figs. 3 and 4. Thereafter the closing of the switch 82 marks the initiation of the cycle, and a predetermined period of time is allowed to elapse before measurement of the current is effected, this time being the equivalent of the period allowed in the previous form for the development of the droplet 35 prior to the measurement of the current thereto. At the predetermined instant a contact 85 is momentarily closed by a cam 86 disposed on the shaft 84. When switch 85 is closed, con-

denser 37a is charged in the manner heretofore described and there appears on the condenser a potential indicative of the rate of flow of current through the fresh surface of mercury at 81 at a predetermined time interval after this electrode has been energized. Immediately following the closing and opening of the switch 85, the switch 82 is permitted to open by the cam 83 and immediately thereafter the cam surface 78 acts to again depress the electrode carrier to dip the surface 81 into the mercury pool 76, again replacing the mercury coating thereon. This construction and mode of operation offers advantages under certain conditions of operation, and by this procedure accurate results are obtained. It will be seen that in general this consists of periodically treating a conducting solid with mercury to provide a periodically renewed surface of mercury thereon and determining the current flowing through said surface under the influence of a predetermined potential at a predetermined time interval after the voltage is applied to the freshly created surface. In this form of the invention a vacuum tube voltmeter such as shown at 38 in Fig. 2 is employed for measuring the potential on the condenser 37a and likewise includes the vacuum tube 38a, cathode exciting battery 38b, plate battery 38c, plate meter 38d and grid leak 38e.

Where it is desired to simplify the circuit of Fig. 5, the cam 83 and switch 82 may be eliminated by shorting out this switch so that the cell circuit is continuous. Potential is then continuously applied to the surface of electrode 81 and the cycle commences at the instant the electrode 81 is separated from the mercury 76. The cam 86 and switch 85 then function to change condenser 37a at a definite time interval after the separation of the electrode from the pool.

In Fig. 6 we have shown a still further form of the invention wherein further means are shown for periodically producing a fresh mercury surface to which a potential is subsequently applied and the current through said fresh electrode surface is measured at a predetermined time interval after the application of the potential. Since the device herein shown is identical with that of Fig. 5 with the exception of the means for the renewal of the electrode surface, only the latter portion of this device will be separately described.

In this form of the invention a fresh drop of mercury indicated by the numeral 88 is periodically produced in the test liquid, voltage is applied thereto and the current flowing a predetermined time after the application of the voltage is measured. While the specific mechanism may take a number of different forms, we have herein shown a glass tube designated generally by the numeral 89 disposed in the form of a U adjacent its lower end so that the end thereof is disposed upwardly with a short arm, the upper end being disposed beneath the surface of the liquid 15 held in the test vessel 14. Here again the test vessel has a pool of mercury 22 disposed in the bottom and forming the reference electrode. The glass tube 89 has a relatively large capillary opening 91 to which mercury flows from a reservoir 92. Disposed in the tube 89 is a valve 93, the valve having a plunger 94 provided with a passage 95 so arranged that when a stem 96 thereon is depressed, the passage 95 will come into registration with the capillary 91 and allow the passage of mercury downward through the tube at a rate such as to substantially instantaneously displace the drop 88 and form a new drop thereto. The valve plunger 95 is promptly returned to its closed position by a spring 97 and is urged to its open position by a cam 98 disposed on cam disk 99 carried on the shaft 84 as described in connection with Fig. 5. Electrical connection is made to the drop 88 by a conductor 101 passing through the side of the glass tube 89 and disposed in the column of mercury in the capillary 91. As described in connection with Fig. 5, rotation of the motor 55 acts to operate the valve 92 to produce a fresh mercury drop at 88. Thereafter the cam 83 operates to close the switch 82 which corresponds in this form of the invention to the initiation of the formation of a droplet as described in connection with the dropping mercury electrode. After the lapse of a predetermined period of time the cam 86 acts to close the switch 83 momentarily, and thereafter the switch 82 opens. Continued rotation of the shaft 84 then causes reaction of the valve and a repetition of the cycle.

As described in connection with the form shown in Fig. 5, the cam 83 and switch 82 may be eliminated from the structure of Fig. 6 and potential continuously applied to the cell, but this procedure and structure is in general less satisfactory than that shown in Fig. 6.

We have found that the area of the drop 88 exposed to the solution 15 is remarkably constant from cycle to cycle so that the determination is always made with substantially the same mercury surface exposed. This procedure has the distinct advantage that the so-called condenser currents observed with the dropping mercury electrode are entirely absent, and that the data obtained thereby are in excellent agreement with theory.

It will be seen that we have provided a new and improved method of making chemical analysis capable of producing greater precision and accuracy than prior art methods.

We have also provided a novel method and apparatus of the type described having greater reliability than those described in the prior art and in which the apparatus is less complicated in use and less expensive to manufacture.

We have also provided a method and apparatus for employing the characteristics of a mercury surface at a selected phase in the life cycle thereof as an index of the characteristics of the test solution in contrast to the less reliable procedure of using the average characteristic over the entire life of the surface.

A further advantage of the invention is that the residual or condenser current is substantially less than with prior art devices, and hence introduces less error in the final result.

A further advantage of our construction employing the dropping mercury electrode lies in the fact that the dropping rate is independent of variations in the voltage applied to the cell, and that the diameter and bore of the capillary and the elevation of the reservoir can be varied within wide limits without affecting the result. This allows for substitution of capillaries of different diameter and length which can be compensated by simple coefficients so that master calibrations can be retained in instances where the capillary tube must be replaced.

We claim:

1. The method of making tests upon a liquid of the type wherein fresh test electrodes are successively exposed to said liquid which includes the steps of starting a flow of current to said electrodes and effecting a measurement of the elec-

trical current to said electrode upon a lapse of a predetermined period of time thereafter.

2. The method of making tests upon a liquid which includes the steps of passing electrical current through a liquid test sample using a recurring fresh mercury electrode as one electrode, and effecting a measurement of the current to said electrode during a predetermined portion of the life thereof.

3. The method of making tests upon a liquid with a dropping mercury electrode which includes the steps of starting the formation of a mercury droplet at a predetermined time, and effecting a measurement of the electrical current to said droplet upon the lapse of a predetermined period of time.

4. The method of making tests upon a liquid which includes the steps of passing electrical current through a liquid test sample using a dropping mercury electrode as one electrode, and effecting an instantaneous measurable response to the current the instant the forming drop has reached a predetermined size in its formation.

5. The method of making tests upon a liquid which includes the steps of passing electrical current through said liquid sample using a dropping mercury electrode as one electrode, starting the formation of a mercury droplet at a predetermined time, effecting a momentary measurable response to the electrical current to said droplet upon the lapse of a predetermined time after its formation, and subsequently discharging said droplet from the electrode after effecting said response to start the formation of a succeeding droplet.

6. The method of testing a liquid which includes the steps of passing electrical current through a liquid test sample using a dropping mercury electrode as one electrode, discharging mercury drops therefrom in rapid succession, effecting a measurement of the current flowing to each of said drops at a predetermined age in the period of its formation, and repeating said measurements on subsequent drops at a plurality of different potentials to establish the data of a current-voltage curve.

7. The method recited in claim 3 wherein the formation of said droplet is started by imparting to the electrode a mechanical shock sufficient to dislodge the previous droplet.

8. The method of making tests upon a liquid which includes the steps of passing electrical current through said liquid using a dropping mercury electrode as one electrode, starting the formation of a mercury droplet at a predetermined time, storing a momentary measurable response to the current to said droplet at a predetermined point in its formation, and thereafter measuring said stored response.

9. The method of making tests upon a liquid which includes the steps of washing an electrode carrier having a solid mercury coated electrode surface with mercury to renew the mercury electrode surface thereon, exposing said electrode surface to said test sample, and effecting a measurement of the current to said electrode at a preselected potential.

10. The method of making tests upon a liquid which includes the step of washing an electrode carrier with mercury to renew the mercury electrode surface thereof, exposing said electrode surface to said test sample, impressing a potential on said electrode, and effecting an instantaneous measurement of the current to said electrode upon the lapse of a predetermined period of time after impressing said potential.

11. The combination in a device of the character described, of a reference electrode and a dropping mercury electrode disposed in a test sample, a circuit for impressing on said electrodes any of a plurality of potentials, means for initiating the formation of a mercury droplet, and means for measuring the current flowing to said forming droplet a predetermined time after said initiation.

12. The combination recited in claim 11 wherein said means for initiating the formation of a mercury droplet comprises means for imparting a mechanical shock to said mercury electrode to shake off the preceding droplet.

13. The combination recited in claim 11 wherein said means for initiating the formation of a mercury droplet comprises a solenoid positioned to impart a mechanical shock to said electrode to dislodge a preceding droplet thereon.

14. The combination in a device of the character described, of a reference electrode and a dropping mercury electrode immersed in a test liquid, a circuit for impressing on said electrodes any of a plurality of potentials, means for effecting a measurable response to the current flowing to a mercury drop on said dropping electrode at a predetermined instant during the period of its formation, means for releasing said drop from said electrode immediately after effecting said response to initiate the formation of a new droplet, and means for actuating the first and second mentioned means in timed relation through continuously recurring cycles.

15. The combination recited in claim 11 wherein the last mentioned means includes a resistance in said circuit through which the current through said cell passes, a condenser connected to opposite sides of said resistance, switch means between said resistance and said condenser for momentarily electrically connecting the same at said predetermined time, and means for measuring the potential on said condenser.

16. The combination recited in claim 11 wherein the last mentioned means includes a resistance in said circuit through which current through said cell passes, a condenser and a resistor in series with said resistance, switch means between said resistance and said condenser for momentarily electrically connecting the same at said predetermined time, and means for measuring the potential on said condenser.

17. The combination in a device of the character described of a reference electrode and a dropping mercury electrode disposed in a test sample, a circuit for impressing on said electrodes any of a plurality of potentials, means including a switch for initiating the formation of a mercury droplet on said electrode means including a switch for measuring the current flowing to said droplet a predetermined time after said initiation, and means for momentarily closing said switches in timed sequence to effect successive measurements.

18. The combination recited in claim 17 wherein said switch closing means comprises a motor driven cam.

19. The combination recited in claim 17 wherein said switches are biased to a normally open position and wherein said switch closing means comprises rotatable cam means positioned to succesively engage said switches to momentarily urge the same to a closed position and a synchronous motor for driving said cam.

20. The combination in a device of the character described of a reference electrode and a

periodically reformed mercury electrode disposed in a test sample, a circuit for impressing on said electrodes any of a plurality of potentials, said circuit having a resistance, a holding circuit of high time constant including a condenser and a resistance in series with said resistance, switch means for momentarily charging said condenser at a predetermined time after said electrode is reformed and a high impedance voltage measuring means for measuring the potential on said condenser.

21. The combination in a device of the character described of a reference electrode, an electrode carrier immersed in a test solution, means for periodically producing a fresh coating of mercury on said carrier to produce successive mercury electrodes, means for impressing a known potential on each of said mercury electrodes, and means for measuring the current from each of said mercury electrodes at a predetermined time after the potential is impressed thereon.

22. The combination recited in claim 21 wherein means is provided for driving each of said means in timed relation through continuously recurring cycles.

23. The combination recited in claim 21 wherein the first mentioned means includes means for immersing said electrode carrier in a volume of mercury to recoat the same with mercury.

24. The combination in a device of the character described of a reference electrode, a drop of mercury supported in a test solution and forming a mercury electrode, means for displacing said drop and substituting successive drops therefor, means for impressing known potentials on said drops, and means for measuring the currents from said drops at a predetermined time after the potential is impressed thereon.

25. The combination recited in claim 24 wherein said drop is supported from below on a nonconducting support having a capillary leading to said drop, and wherein said displacing means includes a mercury reservoir connected to said capillary, a valve for controlling the flow of mercury therethrough, and means for periodically actuating said valve to pass a quantity of mercury sufficient to displace said drop and form a succeeding drop.

26. The combination in a device of the character described of means for forming a fresh mercury surface immersed in a solution under examination, a second electrode electrically connected to said solution, means for applying a difference of potential between said electrodes, and means for measuring the current to said mercury surface at a predetermined time subsequent to the formation thereof.

27. The combination in a device of the character described of means for forming a fresh mercury surface immersed in a solution under examination, a second electrode electrically connected to said solution, means for applying a difference of potential between said electrodes, and means for measuring the current to said mercury surface at a predetermined time subsequent to the application of said potential difference between said electrodes.

28. The combination in a device of the character described of a reference electrode and a dropping mercury electrode disposed in a test sample, a circuit for impressing on said electrodes any of a plurality of potentials, said circuit having a resistance, a holding circuit of high time constant including a condenser and a resistance in series with said resistance, switch means for momentarily charging said condenser at a predetermined time after said electrode is reformed and high impedance voltage measuring means for measuring the potential on said condenser.

29. The combination recited in claim 24 wherein said drop is supported from below on a nonconducting support having a capillary leading to said drop, and wherein displacing means includes a mercury reservoir connected to said capillary.

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