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Rellstab et al.

[11] **3,870,466**

[45] **Mar. 11, 1975**

[54] **METHOD AND APPARATUS FOR AUTOMATIC TITRATION**

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[58] **Field of Search** ..... 23/230 R, 253 R; 204/1 T, 204/195 T; 324/30 C

[56] **References Cited**

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[57] **ABSTRACT**

A method of, and apparatus for, automatic titration of a specimen to be tested, wherein means which causes a reaction with the specimen to be tested, such as a titrating agent or electrical charges for producing a reagent, is discontinuously supplied in individual amounts to the specimen. The variation in time in the value of a measurement parameter characterizing the condition of the specimen is determined. The respective next individual amount of said means is only supplied after the variation in time in the value of the measurement parameter has fallen below a predetermined value.

22 Claims, 6 Drawing Figures

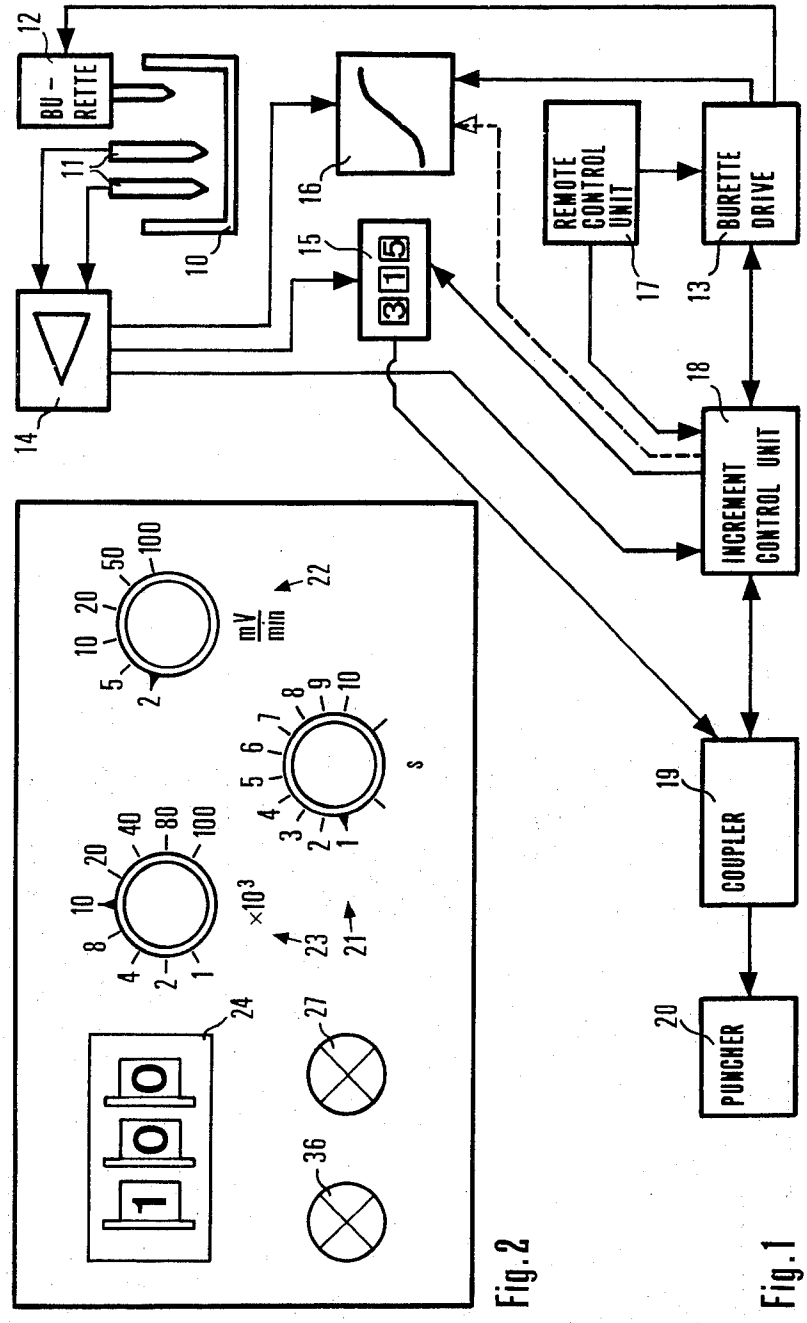
12
BU-RETTE
11
10
16
4
15
315
14
REMOTE CONTROL UNIT
17
BURETTE DRIVE
13
18
INCREMENT CONTROL UNIT
19
COUPLER
20
PUNCHER
22
mV/min
23
×10³
21
s
24
27
36

Fig.2

Fig.1

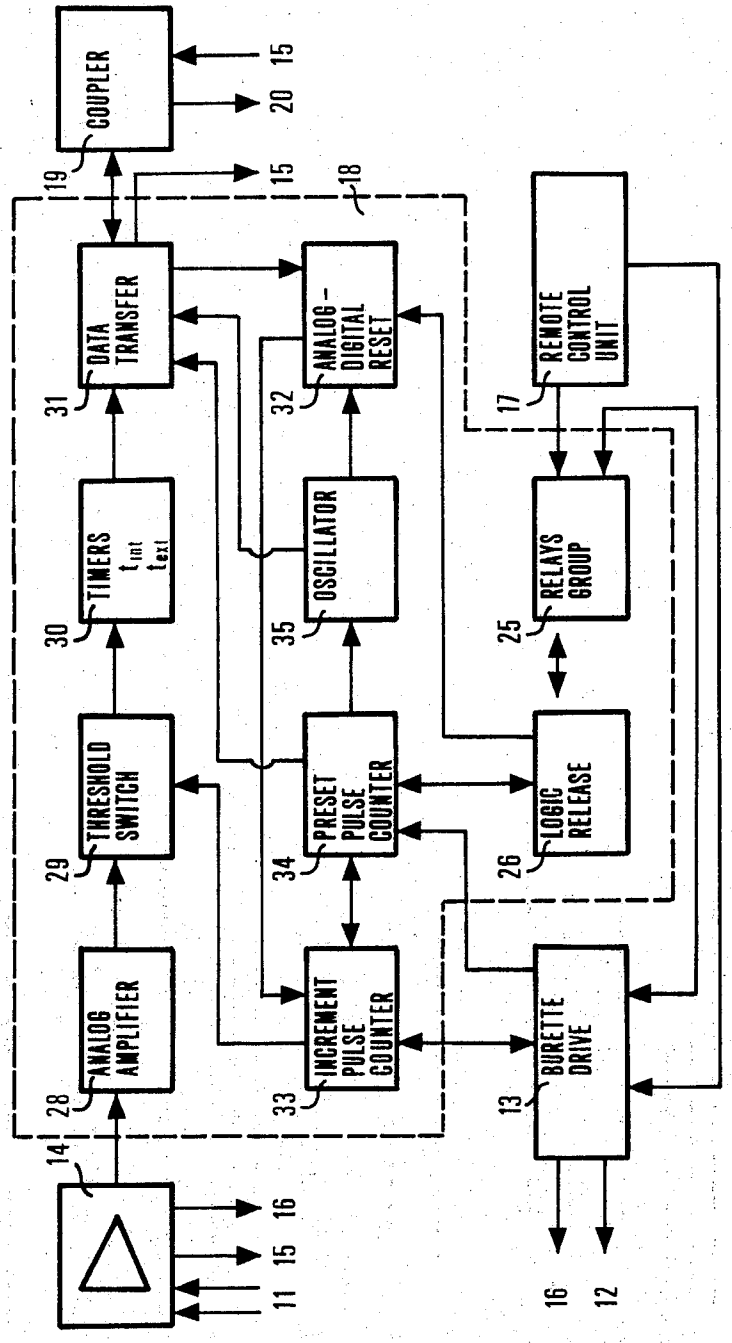
COUPLER
DATA TRANSFER
ANALOG-DIGITAL RESET
REMOTE CONTROL UNIT
TIMERS t_{int} t_{ext}
OSCILLATOR
RELAYS GROUP
THRESHOLD SWITCH
PRESET PULSE COUNTER
LOGIC RELEASE
ANALOG AMPLIFIER
INCREMENT PULSE COUNTER
BURETTE DRIVE
19
15
20
15
18
31
32
17
30
35
25
29
34
26
28
33
13
14
16
15
11
16
12

Fig. 3

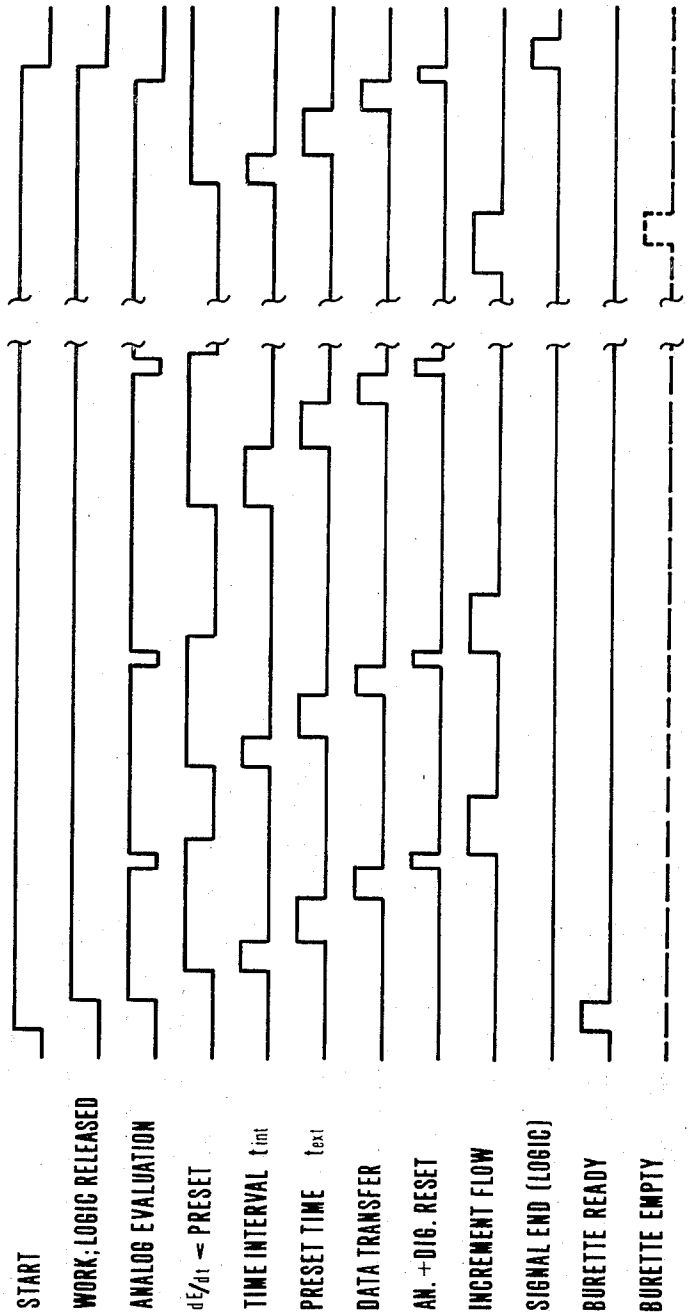
START
WORK; LOGIC RELEASED
ANALOG EVALUATION
dE/dt = PRESET
TIME INTERVAL tint
PRESET TIME text
DATA TRANSFER
AN. + DIG. RESET
INCREMENT FLOW
SIGNAL END (LOGIC)
BURETTE READY
BURETTE EMPTY

Fig. 4

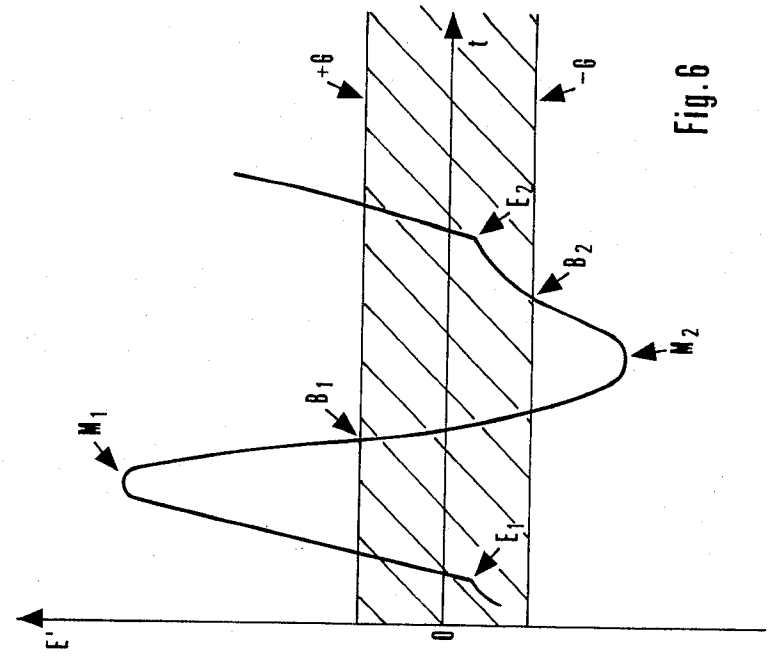

Fig.6

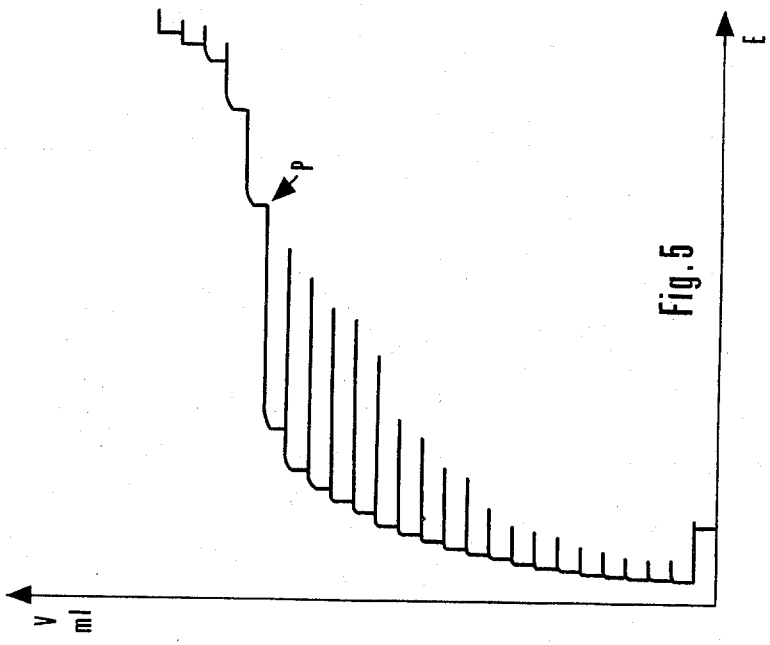

Fig.5

METHOD AND APPARATUS FOR AUTOMATIC TITRATION

BACKGROUND OF THE INVENTION

The present invention relates to a new and improved method for automatic titration, such as volumetric potentiometric titration, and also concerns a new and improved construction of apparatus for carrying out the aforesaid method.

Methods of automatic titration have long been known in the art and are used successfully particularly for neutralization and precipitation reactions in aqueous solution. Generally, automatic titration does not cause serious difficulties in the case of reactions which take place rapidly, with the course of the titration curve being known (for example electrode potential plotted as a function of the volume of added titrating agent).

This is not the case, however, as regards a number of other titration problems, particularly redox titrations which generally occur slowly, titration operations in non-aqueous solution, and titration operations without a precisely known end point. There have been many attempts to automate titration in these cases, but the methods previously proposed in this regard are still not entirely satisfactory. Thus, for example, some potentiometric titration methods have been proposed (Swiss Pat. No. 363,508: Chemische Rundschau No. 35-1969, , pages 639–640) in which a compensation voltage is added to the varying potential of the electrodes. The compensation voltage compensates for the variation in potential caused by an addition of titrating agent, and automatically causes printing of the respective potential and a further addition of agent when the first coincidence occurs between the electrode potential and the compensation voltage (the latter being generated by a motor-driven potentiometer).

Now with the above indicated technique of adding compensation voltages, it is possible only within limits to achieve precise titration curves or the points corresponding thereto. This is so because the follower potentiometers for adjusting the compensation voltage operate only in one direction during one titration, so that compensation can be effected only in the direction of increasing potential (or in the direction of decreasing potential respectively). This presupposes a titration curve in which the gradient does not change in sign, and while this is always correct in theory in the case of potentiometric titrations, it is by far not always the case in practice.

In particular, however, the reason for one shortcoming of the above-mentioned method lies in the operating principle. Each particular point on the curve is determined when the applied compensation voltage has reached the value of the electrode potential at that moment. Further changes in the latter, which occur after such coincidence has been established, remain unheeded, so that in many cases the points on the curve substantially differ from the respective "true" points.

SUMMARY OF THE INVENTION

Hence, it is a primary object of the present invention to provide an improved method of, and apparatus for, automatically titrating a sample in a manner not associated with the aforementioned limitations and drawbacks of the prior art proposals.

Another and more specific object of the present invention relates to an improved method of, and apparatus for, carrying out automatic titration of a specimen or sample wherein the points on the titration curve can be ascertained with a degree of precision which is sufficient for practical purposes and which is considerably better than the previously proposed techniques and equipment for deriving same.

Still a further object of this invention relates to an improved method for automatic titration which can be employed for virtually any titration problems, but especially in redox reactions (a reaction which generally occurs slowly), for titration operations in non-aqueous medium, and in titration operations without a known end point potential, or with a known end point potential which, however, can only be reproduced with difficulty.

Yet a further significant object of the present invention relates to an improved method of, and apparatus for, carrying out automatic titration operations in which there can be obtained both the pattern or course of the titration curve in graphically portrayed form and the numerical values which permit evaluation of the titration by calculation.

A still further object of the invention relates to an improved titration method which allows for carrying out measurements with electrodes having unstable potentials in which it is only necessary to ascertain relative changes in potential within the respective titration operation: and such factor plays a part, for instance, in many ion-sensitive electrodes.

Now in order to implement these and still further objects of the invention, which will become more readily apparent as the description proceeds, the method aspects of this development for automatic titration, considered in their broader aspects, contemplate discontinuously supplying to the specimen to be tested, in individual amounts, constituent which causes a reaction with such specimen, then the next individual amount of such constituent is supplied only after the variation with time in the value of a measurement parameter characterizing the condition of the specimen has dropped below a predetermined value. The constituent which is discontinuously supplied in individual amounts to the specimen can be a titrating agent or electrical charges for producing a reagent.

Not only is the invention concerned with the aforemenioned method aspects but also relates to an improved construction of apparatus for the performance of the aforesaid method, which comprises a reaction vessel having one or more measuring sensing means, means for supplying titrating agent or electrical charges, a measuring amplifier for amplification of the value of the measurement parameter, means for forming the first differential in time of the measurement parameter, means for controlling the supply of titrating agent or electrical charges, said control means being provided with means for comparing the variation in time in the value of the measurement parameter with predetermined value, and means for imparting a supply command to the supply means after the aforesaid variation falls below such predetermined value.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be better understood and objects other than those set forth above, will become apparent when consideration is given to the following detailed description thereof. Such description makes reference to the annexed drawings wherein:

FIG. 1 is a schematic block circuit diagram of an exemplary embodiment of apparatus for the performance of the method of this development:

FIG. 2 is a front view of a portion of the apparatus depicted in FIG. 1:

FIG. 3 is a block circuit diagram of a portion of the apparatus:

FIG. 4 shows in graphic form a time plan depicting the course of the most important functions:

FIG. 5 illustrates a titration curve: and

FIG. 6 illustrates a curve depicting the variation of the potential after the delivery of an individual amount of titrating agent.

DETAILED DESCRIPTION OF THE INVENTION

A typical redox reaction was selected for the purpose of the present description, and specifically the volumetric titration of bivalent iron with permanganate according to the following equation:

$$5\ Fe^{++} + MnO_4^- + 8\ H^+ \rightarrow Mn^{++} + 5\ Fe^{+++} + 4\ H_2O$$

0.01 *n* $KMnO_4$ solution was titrated in increments each of 0.1 ml into an original solution comprising 5.241 g of approximately 0.01 *n* $FeSO_4$ solution. As was found from evaluation of the measured electrode potentials, the equivalence point was reached after the addition of 4.9 ml of titrating solution. A Pt/AgAgCl-electrode in 3 m KCl solution was used as the measuring chain.

The schematically shown arrangement of FIG. 1 was used to carry out the titration operation. A titration vessel **10** contained the specimen to be tested. An electrode measuring chain **11** dipped into the solution — which was continuously and uniformly mixed by a conventional stirrer (not shown) — the electrode measuring chain **11** serving to measure the momentary potential which was dependent on the condition in the solution. A burette **12** supplied the titrating agent or reagent. A burette drive **13,** besides a stepping motor and a variable-frequency pulse transmitter, also included a pulse counter for indicating the volume of titrating agent used (a pulse-controlled piston burette with a stepping motor drive was used, as described in principle, for example, in U.S. Pat. No. 3,319,840 to which reference may be readily made). A measuring amplifier **14** serves for amplification of the electrode potential and for differentiation thereof as a function of time. A digital indicator **15** enables the particular electrode potential to be conveniently read-off, and a recorder **16** serves to record the titration curve. A remote control unit **17** for instance of the type described in Swiss Pat. No. 501,217 was used for starting and for selecting the speed of delivery (pulse or volume per time). Finally, there was provided an increment control unit **18,** a coupler **19** and a puncher **20.**

A portion of the elements diagrammatically shown in FIG. 1 are arranged above one another in the form of a module system in stackable housings, namely the measuring amplifier **14,** the digital indicator **15,** the increment control unit **18** and the coupler **19.** The burette **12** and the burette drive **13** are constructed in the form of a structural unit.

The increment control unit **18** forms an important component of the apparatus according to the invention. Its functions will be described in greater detail hereinafter with reference to the operation of automatic potentiometric titration with the above example, and while referring to FIGS. **2** and **3.** After the specimen to be tested has been introduced into the titration vessel **10** and the burette **12** has been filled with titrating agent (the electronic pulse(=volume) counter now being set to zero), the stirrer is set into operation in order to thoroughly mix the specimen. The following settings are made at the increment control unit **18**: at a rotary switch **21** the time handicap or delay of 1 second for the response time of the measuring system: at a rotary switch **22** the value of the variation in time of the potential 2 mV/min; at a rotary switch **23** the pulse preset or selection, that is to say, selection of the desired number of pulses until the end of the titration operation; and finally, at a multiswitch **24** the number of pulses per increment. This permits a setting between 10 and 990, and in the embodiment illustrated was set at 100; this means that with a pulse preset of $10 \times 10^3 = 10{,}000$, the device cuts out after 100 increments. In the present embodiment the 10,000 pulses correspond precisely to the burette volume of 10 ml; each increment therefore embraces 0.1 ml. The preset pulse counter **34** is designed such that when the preset number of pulses is reached, an increment which may just have been started (for example, as a result of awkward coordination of the number of pulses per increment to the total of pulses), is supplemented to the full number (here 100) of pulses before the "end" signal is delivered. This prevents an incorrect measurement parameter value owing to the delivery of an incomplete increment.

The delivery or infeed speed is set at the remote control unit **17** by controlling the frequency of the pulse transmitter in the burette drive **13,** for example 100 pulses (0.1 ml) in 6 seconds. The apparatus is then started by pressing a start button of the remote control unit **17** and cutting in the mains connection of the burette assembly **12, 13** and the amplifier **14.** This starting pulse causes operation of a first relay of a relay group **25** which forms a galvanic coupling between external elements (**13, 17**) and the increment control unit **18.** After a second relay of the group **25** has received the signal "ready" from the burette drive **13,** then a logic release **26** is operated which takes over the communication between the relay group **25** and the internal electronic assembly of the increment control unit **18,** and the apparatus begins to operate. The condition of operation is signalled by the weak illumination of a lamp **27** on the increment control unit **18.**

A zero measurement is carried out first of all: the potential as measured by the electrodes **11** is amplified and differentiated in the amplifier **14,** the differentiated signal passes the analog amplifier **28** and arrives at the threshold switch **29.** The response value of the threshold switch **29** is determined or controlled by the analog amplifier **28** which can be switched by means of a series of parallel connected resistors, that is to say, the differentiated signal is amplified to a greater or lesser degree according to the desired degree of sensitivity (setting at the rotary switch **22**). If the amplified differentiated signal drops below the predetermined threshold value, then the timers **30** come into operation and determine the length of the delay before the measurement value output. This delay is composed of an internally variable time interval t_{int} and, the adjoining externally set time handicap t_{ext}; t_{int} depends on the magnitude of the variation in potential as a function of time, and at most amounts to 10 seconds, the minimum value being 3 seconds (when the limits of the range are reached, +G and

–G of FIG. 6); t_{ext} is the time handicap or delay as set at the switch **21**, in this case amounts to 1 second.

If after the entire delay time has passed the differentiated signal still lies within the region between +G and –G (the range set at the switch **22**), it is therefore less than 2 mV/min, then by means of the data transfer **31** there is given the signal for measurement parameter value output. The potential supplied by the amplifier **14** is indicated both in the digital indicator **15** and also transmitted by means of the coupler **19** to the tape puncher or perforator **20.** From the beginning of the entry of the differentiated measurement parameter into the region delimited by +G and –G, until transfer of the value of the measurement parameter is concluded, a monitoring lamp **36** (FIG. 2) is illuminated. Then, after the coupler **19** has registered or receipted the data there follows the analog-digital reset, at component **32,** with subsequent starting order for the first increment supply to the increment pulse counter **33,** according to the zero measurement which has now been completed. The increment pulse counter **33** transmits the starting order to the burette drive **13** and at the same time again places into operation the analog evaluation (threshold switch **29**) which was interrupted during the analog-digital reset **32.** During the course of the increment delivery the timers **30** are blocked, in order to avoid premature output of the measurement parameter, for example due to sluggish reaction.

After the increment infeed or delivery is concluded, the cycle described above for zero measurement is repeated, to wit: tracing the pattern of the potential, falling below the threshold value, passing of the time delay, removal of the value of the measurement parameter, reset, delivery of a fresh increment.

If, after the preselected number of pulses, the measurement series has reached the end, then the preset pulse counter **34** supplies a signal which cuts-out the apparatus after the last time delay has expired and the value of the measurement parameter has been taken off. The lamp **27** is now brightly illuminated and in this way visually signals that the titration operation has been completed.

Irrespective of the preselected termination point or end the titration operation can be interrupted at any time, that is to say, the apparatus can be cut-out by actuating the remote control unit **17.**

In another mode of operation of the apparatus where there is no punching of the measurement parameter values or no receipting by the coupler, an oscillator **35** assumes the function of again cutting-in the analog-digital reset **32.**

FIG. **4** illustrates the essential steps of the individual measuring operations in the form of a sequence diagram. The correlation of the individual phases described above will be recognised.

Experience has shown that it can occur that a titration operation is started although, for example, the amount of titrating agent present in the burette is no longer sufficient to conclude the titration operation. In order to take this and similar operating errors into account the invention contemplates that unintentional termination of the supply of titrating agent (or electrical charges) to the specimen automatically ensures that the particular value of the measurement parameter is no longer digitally indicated and/or registered. In this way measurement values which are not produced, for example, after the correct addition of titrating agent, cannot be used to calculate the particular parameter being sought.

The lowermost broken line FIG. **4** therefore also illustrates a "burette empty" signal which will occur if for any reason (for example operating error) the preset volume exceeds the amount still contained in the burette; after the remainder of the burette contents has been titrated to the vessel **10,** the signal burette empty which is to be delivered by the burette drive **13** and transmitted by way of the preset pulse counter **34** to the data transfer **31,** causes the measurement to be immediately interrupted and the apparatus to be cut out, without the started increment producing a measurement parameter value. This not only prevents that an incorrect value of the measurement parameter will be produced, but also ensures that there is no recording of "dummy" measurement parameters, which are not preceded by an increment delivery (apart from zero measurement at the beginning of the measurement series).

The function of graphic recording of the measurement parameter values is performed by the recorder **16** connected to the measurement amplifier **14** and the burette drive **13** (it can also be connected to the increment control unit **18,** instead of to the measurement amplifier **14,** as generally shown in FIG. **1** by a broken line). A typical curve is portrayed in FIG. **5** in which the delivered volume V is plotted in ml as a function of the potential E. Only a small number of increments are illustrated for the sake of clarity. FIG. **5** clearly shows the step form which is characteristic of the present method and the large jump in potential at the equivalence point P.

FIG. **6** diagrammatically shows one form of the course or pattern of the curve of the potential E' differentiated in time as a function of the time *t*. The preselected range for the variation in time, which range is delimited by +G/–G (in the above example: ±2 mV/min) is illustrated by a hatched area. There will be recognized the point E_1 of the beginning of an increment delivery, followed by a rapid rise in the potential change up to the positive maximum M_1, to which corresponds an internal time delay t_{int} of about 8 seconds. This is followed by a rapid potential reversal, until the region at B_1 is reached for the first time. Here the rest of the time t_{int} is either still 3 seconds (minimum time) when more than 5 seconds has passed since the maximum M_1, or if, for example, only 3 seconds have passed since M_1, the remaining time is 5 seconds. The external time handicap t_{ext} would thereafter have to expire before the value of the measurement parameter could be removed or taken-off. Since, however, the variation in potential has already moved out of the hatched region in the negative area, before $t_{int} + t_{ext}$ has passed, then when the limit –G, that is to say, the threshold switch **29,** is exceeded, both timers **30** have been reset and the delay began anew. At the minimum M_2, t_{int} is about 5 seconds; after about 4 seconds, the limit –G is again reached. The variation in potential, which is now significantly slowed, is still in the region with (±) 2 mV/min after the passing of $t_{int} + t_{ext} = 3$ s (minimum value) + 1 s = 4 s, and the value of the measurement parameter is now removed and, after analog-digital reset which requires about 0.5 second, a new increment is delivered at E_2 and thus a new cycle begins.

Because of the dependency of t_{int} upon the maximum variation in potential there is taken into account the fact that rapid and large variations frequently occur in

the specimen which change the sign. There is thus the danger that with an insufficient time reserve a measurement parameter would be registered, although the variation again subsequently leaves the set range +G/−G; therefore an incorrect measurement parameter would be recorded.

The method provides equilibrium titration; only when the value of the differential quotient of the value of the measurement parameter versus time is lower than a predetermined value, that is to say, a good approximation to a condition of equilibrium is established in the specimen to be tested, is the next amount of titrating agent supplied (or produced).

The mode of operation of the self-controlling method according to the invention was described above with reference to a volumetric potentiometric titration operation, which gives a potentiometric indication of the course of the reaction, but in principal other methods of indication also can be used, for example, conductometric, voltametric, amperometric, photometric or thermometric titration operations can be performed with the present method. As the particular characteristic measurement parameter (conductivity, current strength, transmission, temperature, etc.) is usually converted into an electrical voltage for reasons of measuring technique, the term measurement parameter generally used in connection with the method described above also always signifies an electric voltage corresponding thereto.

It is preferred for the discontinuous supply to be effected, at least over a part of the titration operation, in equal individual amounts, since the supply of equal individual amounts or increments affords the substantial advantage that evaluation by calculation of the individual points on the curve, for example by means of desk computers, is greatly simplified.

So that the method can be adapted to the circumstances of different titration operations, the size of the respective individual amounts of titrating agent or electrical charges to be supplied is preferably adjustable. It is also of advantage for the predetermined value of the variation in time in the value of the measurement parameter to be adjustable; in this way, it is possible to achieve an approximation according to the particular problem encountered, which is virtually as precise as may be desired to the particular condition of equilibrium.

It will be noted that the removal or pick-up of the measurement parameter value is preferably such that, before the commencement of each operation of supplying an individual amount, the respective value of the measurement parameter is indicated and/or registered in an analog and/or digital manner. In the case of analog registration the volume of titrating agent is indicated by means of a recording pen for example on the abscissa, while the particular potential measured is entered on the ordinate (as shown in FIG. 5); in that case, the paper feed is synchronised in known manner with the supply of titrating agent, for example by a drive by means of two synchronously moving motors.

It is also preferred for the particular value of the measurement parameter to be indicated and/or registered only after at least one time interval has passed since the preceding supply of an individual amount of titrating agent. The length of the time interval depends upon the maximum value of the particular variation in time of the measurement parameter, but without falling below a given minimum value, and its number being influenced by the frequency with which the variation in time in the value of the measurement parameter passes through the region delimited by the predetermined value. This facet of the method takes account of the fact that in many cases the variation in the measurement parameter must first "swing in" or oscillate about a value before a condition of equilibrium is established, that is to say, the variation for example experiences a rapid increase, then falls back and assumes a negative value, and so forth. The above mentioned step avoids premature removal or pick-up of the measurement parameter.

According to the nature of the employed measurement sensing means and the mixing in the titration vessel it can occur that a certain time passes, after the addition of the titrating agent, before a variation in the value of the measurement parameter can be measured. This is particularly the case for electrodes with a certain response inertia. Thus, in order to be able to also take these factors into account, the response time of the measurement system is taken into account by the selection of the additional time handicap or delay.

The titration method described above can adapt its time requirement exactly to the particular condition, that is to say, measurement parameter values of virtually any desired precision are fully automatically produced without requiring an excessive amount of time. The inventive method makes it possible to determine precise values even when the nature of the titration curve is unknown, in other words without empirical date, and so-to-speak to titrate blind. The conventional principle of manual operation is followed: delivery of titrating agent, waiting, reading-off, noting, delivery, and so forth. The method is virtually universal in application and, particularly when operating with uniform increments within each titration operation, it is highly suitable for connection to electronic data processing means, for example for the determination by calculation of the equivalence points in accordance with one of the known methods (for example, the Kolthoff or the Fortuin methods).

It is obvious that instead of the potentials, as in the above described example, p_H− or any other suitable p_x−values can be determined.

Another possible use of the method is building up process controls by the connection of suitable elements.

The method is suitable not only for carrying out volumetric titration operations, but is likewise applicable to coulometric procedures in which a reagent performing the function of the titrating agent is formed in the specimen by supplying electrical charges, and the number of charges supplied is monitored.

While there is shown and described present preferred embodiments of the invention, it is to be distinctly understood that the invention is not limited thereto but may be otherwise variously embodied and practiced within the scope of the following claims. Accordingly,

We claim:

1. A method for the automatic titration of a specimen to be tested, comprising the steps of discontinuously supplying in individual amounts to the specimen a constituent which causes a reaction with the specimen, determining the variation in time in the value of an electrical measurement parameter characterizing the condition of the specimen, and supplying a respective next

individual amount of said constituent only after the variation in time in the value of said electrical measurement parameter has entered a preselected range.

2. The method as defined in claim 1, including the step of discontinuously supplying in individual amounts a titrating agent serving as said constituent.

3. The method as defined in claim 2, including the step of discontinuously supplying the titrating agent in equal individual amounts at least over part of the titration operation.

4. The method as defined in claim 3, further including the step of adjusting the size of the equal individual amounts of the titrating agent.

5. The method as defined in claim 1, wherein the preselected range is adjustable.

6. The method as defined in claim 1, including the step of setting a predetermined time delay in order to take into account the response time of the measuring system.

7. The method as defined in claim 2, further including the step of visually displaying the respective value of the electrical measurement parameter prior to the commencement of each operation of supplying each said individual amount of said titrating agent.

8. The method as defined in claim 7, further including the step of visually displaying the respective value of the electrical measurement parameter only after at least one time interval has passed since the preceding supply of one said individual amount, the length of said time interval being governed by the maximum value of the particular variation in time in the value of the electrical measurement parameter, but not falling below a given minimum value, and its number being determined by the frequency with which the variation in time of the value of the electrical measurement parameter passes through said preselected region.

9. The method as defined in claim 7, further including the step of automatically preventing display of an electrical measurement parameter value upon premature termination of the supply of titrating agent to the specimen.

10. The method as defined in claim 2, further including the step of registering the respective value of the electrical measurement parameter prior to the commencement of each operation of supplying each said individual amount.

11. The method as defined in claim 10, wherein the registration of the respective value of the electrical measurement parameter occurs only after at least one time interval has passed since the preceding supply of one said individual amount, the length of said time interval being governed by the maximum value of the particular variation in time in the value of the electrical measurement parameter, but not falling below a given minimum value, and its number being determined by the frequency with which the variation in time of the value of the electrical measurement parameter passes through said preselected region.

12. The method as defined in claim 10, further including the step of automatically preventing registration of the electrical measurement parameter value upon premature termination of the supply of titrating agent to the specimen.

13. An apparatus for the automatic titration of a specimen to be tested, comprising a reaction vessel for the specimen and having at least one measuring sensing means, means for discontinuously supplying individual amounts of a titrating agent to the specimen, a measuring amplifier for amplification of the value of an electrical measurement parameter characterizing the condition of the specimen, means for forming the first differential in time of the electrical measurement parameter, means for controlling the supply of titrating agent, said controlling means incorporating means for comparing the variation in time in the value of the electrical measurement parameter with a preselected range, and means imparting a supply command to said supply means after said variation has entered said preselected range.

14. The apparatus as defined in claim 13, further including means for setting said preselected range.

15. The apparatus as defined in claim 13, further including means for setting the size of the individual amounts of the supply of titrating agent.

16. The apparatus as defined in claim 13, further including means for selectively time delaying a response time of the apparatus.

17. The apparatus as defined in claim 13, further including means for visually displaying a respective value of the electrical measurement parameter before the beginning of the supply of each individual amount of titrating agent.

18. The apparatus as defined in claim 17, further including means for producing at least one variable time interval between the first variation in the value of the electrical measurement parameter falling below the preselected range and the indication of the respective value of the electrical measurement parameter.

19. The apparatus as defined in claim 17, further including means for automatically preventing further display of the value of the electrical measurement parameter when the supply of titrating agent to the specimen is prematurely terminated.

20. The apparatus as defined in claim 13, further including means for registering a respective value of the electrical measurement parameter before the beginning of the supply of each individual amount of titrating agent.

21. The apparatus as defined in claim 20, further including means for producing at least one variable time interval between the first variation in the value of the electrical measurement parameter falling below the preselected range and the registration of the respective value of the electrical measurement parameter.

22. The apparatus as defined in claim 20, further including means for automatically preventing further registration of the value of the electrical measuring parameter when the supply of titrating agent to the specimen is prematurely terminated.

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