AN AUTOMATIC TITRATOR
USING ELECTROLYTICALLY GENERATED TITRANTS

By

W. N. Carson, Jr.
Analytical Research
Analytical Unit

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INTRODUCTION

The purpose of this report is to present some design and construction data for automatic titrators.

The aim of the titrator program was not to develop an universal titrator, but to make available suitable components and units so that a "tailor made" instrument is available for each type of titration. Tailor made titrators offer several advantages over universal type titrators: only those features necessary for the titration to be performed need be put in the titrator; conversely, special features too little used for incorporation in universal type titrators can be added.

One type of titration may utilize all the operation time of the titrator; obviously, the universal type offers no advantages, except possibly initial cost, in this case. The cost of the tailor made instrument is greatly lessened by the use of standard units to make up the bulk of the titrator.

After a survey of the automatic titrators described in the literature, it was decided that the principal limiting factor in their operation was the use of standard solutions which require rather complex or delicate mechanisms to control their delivery. The decision was made at the start of the program to concentrate on the use of electrolytically generated titrants in place of standard solutions.

The use of electrolytically generated titrants for analysis has been well established in recent years by the investigations of various workers in the field of coulometric analysis. This work has shown that a wide variety of useful titrants can be generated, including cerate (8), bromine (13), ferrous ion (4), cuprous ion (10), titanous ion (5), acid (6), and base (3). The generation of titrants by electrolysis means that the
"standard solution" of a titrator using this method is an electric current which can be used to generate any of the reagents for which a suitable electrolysis scheme has been developed. This generation of reagent is particularly attractive when it is remembered that the control of the titrant resolves into the control of an electric current, which is relatively simple compared to the precise control of liquid flow from a buret or syringe.

The useful features for microtitrations of coulometric methods are: the rate of addition of titrant can be as low as $10^{-11}$ equivalents per second and still be more accurately measured than can delivery from a buret, and no dilution of the sample need occur during the titration. Normally, rates of $10^{-9}$ equivalents per second are the lowest used; this is a titration using 0.1 milliampere, and is equivalent to a flow of one microliter per second of an 0.001 normal standard solution. Recently, Deford, et al. (6) and Reilley, et al. (11) have shown that coulometric titrations can be carried out in the 100 milliampere range. This permits titration of macro samples.

A few automatic titrators using electrolytic generation of reagent have previously been described. Shaffer, Briggio, and Brockman (12) have described an instrument for the automatic titration of certain contaminants in gases. A commercial device, the Titritlog (Consolidated Engineering Corporation, Pasadena, California), for the same titration is available. Deford, Johns, and Pitts (7) have described an automatic stopping device for coulometric titrations.
SUMMARY

An automatic titrator which is suitable for performing microtitrations and which uses electrolytically generated reagents has been developed. The reagents are generated in suitable electrolysis cells at a constant current, which can be varied from 0.1 to 15 ma. (10^-9 to 1.5 x 10^-7 equiv/sec). End points are detected by use of a modified line-operated pH meter which permits the use of either potentiometric, polarized, or glass electrode systems. An output signal from the pH meter operates a trigger circuit that, together with several auxiliary circuits, controls the titration. The auxiliary circuits permit the delay of the start of titration until the proper temperature for titrations is reached (for titration at elevated temperatures), the introduction of anticipation of endpoint control (to prevent over titrations) and duration of endpoint timing circuits. The general design and features of the circuits are discussed, and the specific design for an automatic uranium titrator is given.

DESCRIPTION OF TITRATOR COMPONENTS

General

The titrator is composed of three major parts: power supply, controller, and titration assembly. Of these, the power supply contains most of the functions needed for all titrations, while the controller and titration assembly contain the remainder of the functions both general and specific for a given titration. The division is somewhat arbitrary, and could be changed if desired. The power supply is the most costly part, and provision can be made to use one power supply in more than one titrator, which, to avoid confusion, will be referred to in this discussion as a titration set up. Because the titrant delivery system is essentially an electric circuit, the problem of using one power supply for more than one titration set-up is solved by using a multiple switch in the power supply to connect as desired the appropriate controller and titration assembly. Although there is no theoretical limit to the number of set-
ups that can be accommodated by one power supply, the use of an automatic titrator implies a heavy load for particular titrations. Thus it is probable that two to four set-ups are all that can be efficiently used, i.e., the two to four set-ups would require all the time of use of the power supply. A maximum of four set-ups is considered by the author as the feasible upper limit. In many cases one set-up per power supply would be justified.

Figure 1 gives a block diagram of a titrator. Each of the three major parts is composed of several subunits. Thus the power supply includes: a constant current source to supply the titration current, a trigger circuit - pH meter combination to detect endpoints, a precision electric timer to measure the length of time of generation of current, and the standardizing circuit to determine the value of the electrolysis current. The controller contains, depending upon the particular titration, a trigger output circuit which controls the electrolysis current and the stop watch current, an anticipation circuit which is used to prevent overshooting of the endpoint, a duration of endpoint circuit which times the duration of an endpoint and acts to stop the titration when the time of the endpoint duration exceeds a set value, heating control when the titration is conducted at an elevated temperature, and such other controls as necessary. The titration assembly contains the titration cell, stirrers, heaters, the electrolysis electrodes, the indicator electrodes, and the special pretreatment and titration auxiliary equipment.

Power Supply. Figure 2 gives the block diagram of the power supply. This may or may not be constructed in a single unit; each of the parts is essentially an independent unit in construction. The single unit requires less space and interconnections than does the "breadboard" or multiple unit model. As shown, the power supply is composed of the constant current source, the potentiometer-calibration resistance system, the pH meter, the trigger, the electric stop watch, and the multiple input-output switch. Each will be described below.
The constant current source is essentially the same as one described previously (1), but differs in several details. Figure 3 gives the wiring diagram of the unit. The panel meter M is a low limit contact meter and serves as the sensing element for an interrupted current during titration. An interruption of the current is almost always caused by an open circuit in the generator electrode system (a bubble in a salt bridge is frequently the cause), which causes the current through the meter to drop to a low value. The contact of the meter, when energized by a drop in the meter current, locks in an alarm circuit to warn the operator that an interruption has occurred. The reference resistances $R_1, R_2$ are wire wound potentiometers. Provision is made for inserting extra fixed resistance into the reference system at jack J-1. This permits setting the constant current source to currents down to approximately 0.1 ma.

The calibration resistance is a precision resistor placed in the output of the constant current source at J-2 (Figure 3). Various resistor values up to 1000 ohms can be used. The IR drop across the calibration resistor is measured by use of a potentiometer. With low resistance external circuits, this calibration need be done only a few times per shift, unless of course, the current is changed deliberately. The current of the constant current source can be set to a factor value, as described elsewhere (3, 2). The use of factor currents in effect puts a calculation mechanism in the titrator which simplifies the work in the routine laboratory.

The pH meter used is a modified Beckman model H-2 meter. The modifications are made to supply a low impedance input for the trigger and consist of alterations to the feed back loops of the pH and mv circuits. The wiring diagram is given in Figure 4. In the pH circuit, a 150 ohm resistance is replaced by a 17.5 ohm ($R_1$) and 132.5 ($R_2$) ohm pair, and a 0.476 ohm resistance is inserted as $R_3$. The change in the mv circuit is the insertion of $R_4$ and $R_5$. The signals developed across the resistances are led by shielded cable to the input of the trigger circuit. The
remainder of the pH meter circuit is not changed from the manufacturer's wiring. The modification does not interfere with its normal use and correct pH and mv indications are obtained whether the trigger is used or not. If the pH meter is to be incorporated in a single unit power supply, the leads to it, and the circuit itself must be adequately shielded.

The trigger is essentially a switch that operates at a selected potential of the indicator electrodes. Figure 5 gives the basic circuit for such a device. The potential developed by the indicating electrodes is amplified in the pH meter, and a signal proportional to this potential is created across the resistance networks inserted in the pH meter by the modification described above. The signal voltage is compared with a voltage from a potentiometer, and the difference in polarity and magnitude appear as a deflection in the galvanometer switch. The comparison voltage of the potentiometer can be set at a potential which is equal to that developed by the pH meter at the endpoint of the titration. During the course of a titration, the potential difference between the potentiometer and the pH meter signal decreases until the endpoint potential is reached (by the indicator electrodes) and then reverses in polarity and increases. The decrease, reversal, and increase of potential are followed by the galvanometer switch which at the endpoint opens one contact and closes the other. However, a certain amount of potential difference must exist before the contacts are made or broken; this gives rise to a dead space in the trigger which should be as small as possible. Due to the almost complete voltage degeneration of the circuits used in the pH meter, the output signal for full scale deflection of the pH meter is only a few millivolts. This makes desirable the use of an amplifier in order to decrease the dead space.

Inasmuch as recorder amplifiers, especially the Brown "Electronik", are in many respects similar to galvanometers, it is feasible to replace the galvanometer with such an amplifier. This was done in the trigger used. Figure 6 gives the circuit. One input lead from the pH meter
is connected to one side of the slidewire (R-1) and the other to one side of
the Brown amplifier input. The other amplifier input is connected to
terminals used to insert anticipation (see below) and then onto the slide
of the slide wire. The complex switching arrangement is required be-
cause the trigger is to be used on both pH and mv ranges. The span
voltage across R₁ is obtained by suitable adjustment of R₂ and R₃. Only
the first three amplifying stages of the Brown Amplifier are used, to-
gether with the halfwave rectifier circuit. This part of the circuit is
unchanged from the manufacturer's design. The output from the final
stage is a 60 cycle alternating voltage, either in phase or 180° out of
phase with the 110 volt line voltage, depending upon the polarity of the
two leads to the chopper. The amplification factor is quite high, and the
amplifier saturates (achieves maximum output) with microvolt inputs.
The signal from the amplifier is used to control a 2050 thyatron. By
using an alternating plate voltage in phase with the line voltage, the
thyatron enables the circuit to detect the polarity of the input signal.
This is because the tube will conduct only when the signal from the ampli-
fier and the plate voltage are in phase and will not conduct if they are out
of phase. However, the straight application of the amplifier signal to the
grid of the thyatron is not suitable, because the bad wave form of the
signal permits several triggering points in the firing cycle. A bias
circuit is therefore used which introduces a phase shifted voltage into
the grid-cathode circuit such that only one triggering point occurs --
one near the peak of the plate and grid voltage positive swing. The out-
put of the tube controls a mechanical relay which actuates the trigger
contacts.

The electric stop watch used is the Model SM60 of the Standard
Electric Time Co. The multiple switch used is, of course, dependent
on the number of set ups desired and can be made up of ordinary wafer
units, except for the pH meter leads and the anticipator leads which should
be shielded.
The power supply must be carefully wired. It is important that the pH meter and leads be carefully shielded and that stray capacities and coupling be avoided in the remainder of the units. The constant current source must be allowed to float; it is grounded via the titration cell. If it is grounded elsewhere, a spurious signal is developed in the pH meter, usually driving it off scale. WARNING! An open circuit in the constant current source output develops high (300 V) voltages at the break which should be considered when making adjustments. All the units described here have been tested in continual service for over 6 months and have operated without maintenance, other than replacement of tubes.

Controller. As stated above, this part of the titrator is designed specifically for a particular titration. The controller, like the power supply, is a unit comprised of several separate parts. Unlike the power supply, only a few parts are common to all titrations. These are the trigger output relay circuit which controls the titration current and electric stop watch current, the duration of endpoint timing circuit which allows the controller to determine in a positive manner that the titration is complete, and the titration lock-out circuit which shuts off the titrator at the end of the titration and prevents further addition of electrolysis current until a reset circuit is operated. In addition to the above, other auxiliary circuits are used when the nature of the titration calls for them. These are the anticipation circuit, used to trigger the titrator before the endpoint to prevent over titration; a heater control circuit, used when the titration must be conducted at an elevated temperature; and stirring controls.

The trigger output relay system is given in Figure 7. Several precautions are necessary for satisfactory operation: the constant current must either be shorted or connected to the titration cell, i.e., there must not be an open circuit in the constant current circuit; the electrode with the lowest impedance (in the titration cell) to the sensitive indicating
electrode must always be connected to the constant current source; and 
the polarity of the filter condensers must be carefully observed. A con-
denser capable of withstanding about 900 volts is necessary; the conden-
sers arrangement is the one used by the author. The two relays are used to 
obtain the “make before break” action required by the constant current 
circuit. A single relay can be used if the contacts operate in the re-
quired manner. The connection to the trigger is determined by the 
nature of the endpoint which determines whether the trigger relay opens 
or closes at the endpoint. The other contact is used to activate other 
circuits such as the endpoint timing circuits, or the anticipation circuit.

The use of a duration of endpoint timing circuit permits the 
titrator to be used in titrations with transient endpoints and also per-
mits the titrator to determine the end of the titration without ambiguity.
A convenient time delay circuit for titrator use is given in Figure 8. 
This is a conventional RC time delay circuit which is reset whenever 
the trigger opens the relay operating the circuit. Change of R gives a 
range of time values which are set to exact values by means of R2.

The timing accuracy is sufficient for titrator use. The output of the 
timing circuit normally operates a lock-out circuit (shown) and indica-
tor. The reset switch is used to open the circuit of the lock-out relay, 
restoring the power to the relay network.

In many titrations a lag, or slow response of the indicator 
system, makes the titrator tend to overshoot the endpoint by signifi-
cant amounts. This is because the triggering point must be set at 
the endpoint of the equilibrium potential curve, whereas in the titration, 
the instantaneous potential of the indicator electrodes which develop 
the signal to the trigger is markedly lower than the equilibrium po-
tential. It is difficult to allow for the overshoot by downward adjustment 
of the triggering point, hence some form of “anticipation” of the end-
point must be used for these titrations if precise values are to be ob-
tained.
A few titrations show such anticipation. In these, the instantaneous potential of the indicator system is always greater than the equilibrium potential. The titrations are generally characterized by a hesitant, or tentative approach to the endpoint, with smaller and smaller increments of titrant being added at longer and longer intervals. This tentative approach prevents overshooting.

The behavior of the two indicator systems is shown in Figure 9. Curve #1 is representative of the anticipating indicator system; curve #2 is representative of the lagging indicator system. The instantaneous potentials more or less rapidly approach the equilibrium potential if the addition of titrant is stopped and are not exactly reproducible.

The points X show where the trigger will first cut off the addition of titrant under automatic titrator conditions. The lagging indicator system continues to increase in potential so only one cut-off is obtained, and the cut-off appears too late, and the sample is overtitrated. The behavior of a titration with anticipation is somewhat more complex. After a cut-off, the indicator potential starts to decrease, and the trigger starts the addition of titrant again. The addition of titrant continues until the instantaneous potential goes above the triggering point again. The trigger then cuts off the titrant addition, and the cycle is repeated until the last increment of titrant drives the equilibrium potential past the endpoint potential. This behavior is shown in Figure 10. In this diagram the instantaneous potential curve is shown as a solid line, and the equilibrium potential curve is shown as a dotted line. As can be seen, a number of preliminary trigger points are obtained before the final trigger point is reached. The potential at the end of a titration is always a few millivolts above the endpoint potential, as would be expected from the nature of operation of the trigger. This represents a very slight excess of titrant, usually less than that equivalent to 0.01 minute of generation time.
It is thus seen to be desirable to have the indicator system be an anticipating type. The purpose of the anticipator circuit is to convert lagging type indicator systems into anticipating type systems. This is done by inserting in the trigger circuit an opposing voltage to the reference potentiometer voltage which has the effect of lowering the triggering potential. The amount of lowering used is dependent on how much anticipation is necessary. The action of the anticipator circuit is to decrease this inserted voltage, i.e., the triggering potential is increased whenever the titrant addition is stopped. Eventually the inserted voltage is decreased to zero. Figure 11 gives an anticipation circuit the author has used.

The action of the circuit is as follows. At the start of the titration, the full IR drop across the variable resistor R-1 is impressed on the trigger input. When the trigger cuts off the addition of reagent, the controller relay starts the motor M into rotation, which decreases the value of the variable resistor R until the trigger opens the controller relay. Limit switches shut off the motor at either end of the rotation. The value of the inserted potential is adjusted by R-2; the rate of decrease is governed by the speed of motor M. Other circuits can be used for anticipation; these are somewhat complex electrically but usable. Haves, Strickler, and Peterson describe such an anticipation network used in a commercial model titrator (8). The reset circuit is used in conjunction with the reset control of the lock-out relay.

For microtitrations at elevated temperature, the use of thermocouples to regulate the temperature is recommended. Iron-constantan thermocouples used with a "Simplytrol" Controlling Pyrometer (Assembly Products Co., Chagrin Falls, Ohio), offer a simple and accurate means of controlling the temperature. The pyrometer sensitive element is a meter relay with a heavy duty output relay. Automatic titrations call for automatic control of the temperature.
The description of the uranium titrator will give a detailed plan of a controller.

**Titration Assembly.** This third major part is the least standardized unit. The essential requirements are a means for efficient stirring, a generator electrode system, and an indicator electrode system. The latter is conventional, comprising a sensitive electrode and a reference electrode, and offers only the difficulties associated with the particular system. The generator-electrode systems used vary from titration to titration and are either systems in which the electrodes are both in the sample solution during electrolysis, or a system in which the electrodes are separated by a salt bridge. The latter is the most common. The resistance of the generator system should be as low as possible, preferably only 1000 to 2000 ohms. This requires short, large cross section bridges. The author has found 1/4" in diameter (internal) by 1/4" bridges are best. The plug is saturated salt (KCl or NH₄NO₃) -agar-agar for unheated titrations and sulfuric acid-silica gel bridges for heated titrations. Neither is entirely ideal, but both have a reasonably long life under continuous use.

Stirring is important since it affects the response of the indicator. Either magnetic or motor stirrers may be used. In the latter case it is possible to use the stirrer as one of the generator electrodes provided the shaft is insulated from the motor and is not grounded. A convenient heater for titrator use is the Fisher Hotspotter heating element (Fisher Scientific Company Catalog # 11-502-15 which screws into an ordinary lamp socket. It can withstand full line voltage, and the heating can be controlled by a 100 ohm 100 watt series resistance (Ohmite 0457). The other titration requirements, such as inert gas blanketing, pretreatment of sample, etc., are conventional and need not be described.

**Discussion**

The titrator components described above can be used in other
types of titrators. In use, the pH meter has proven the limiting factor in stable operation. A battery operated pH meter might be more stable but is too cumbersome for

Most of the experience to date has been with an uranium titrator which is discussed below. Other titrators are being designed for use in acid-base titrations and for plutonium titrations.

DESCRIPTION OF URANIUM TITRATOR

General

The automatic titration of uranium is based on the oxidation of U(IV) to the U(VI) by means of electrolytically generated ferric ion. The chemistry and procedure are given by Carson. (2) From an instrumental point of view, the titration shows an anticipation of endpoint behavior (the indicator potential leads the equilibrium potential). The solution must be titrated at elevated temperature under an inert gas blanket.

Description

The power supply presently used is a breadboard unit. A single unit is planned which will permit 4 set-ups. The components of the breadboard (and single unit) are the same as described above. The controller circuit is given in Figure 12. This controller performs the following functions: 1) it prevents the titration from starting until the sample is heated to the operating temperature; 2) it controls the heating so that the sample remains at 85°C during the titrations, and 3) it includes the trigger output and endpoint timing circuits described above.

To start a titration, the "Titrate" switch is closed. The controller will now permit the heating current, but not the titration current, to flow. The sample temperature is controlled via a "Simplytirol" pyrometer (indicated in Figure 12 by a box) whose input is an iron-constantan thermocouple immersed in the titration cell. The heater line is
connected to the normally closed side of the Simplytrol output relay and relay L-1 to the normally open side. When the sample reaches the operating temperature, the Simplytrol relay closes the circuit to L-1 and opens the heater circuit. Relay L-1 locks in electrically, and further action of the Simplytrol relay controls only the heater current to maintain the proper temperature of titration. The closing of L-1 supplies power to the trigger relay circuit which will then close either L-2 or L-3. If the potential of the titration solution is above the cut-off potential set on the trigger, L-3 is closed, and the titration continues. When the trigger cuts off, L-2 closes, and the timing of the endpoint begins. The action in the uranium titration is that of the anticipatory endpoint described above. Relay L-5 provides the lock-out circuit for the device and resets whenever the "Titrate" switch is opened.

Details of the titration assembly, procedure, and results are given in another report (2).

Discussion

Most of the early instrumental difficulties were caused by failure of the indicator electrode system and the generator salt bridges. These difficulties have been solved, and instrumental troubles are rare.

CONCLUSION

The design and operation of elements of an autotitrator using electrolytically generated titrants has been described. The design is for microtitrations, but most of the components could be used for macrotitrations as well. Further work is being done on these components, but they are now in an advanced state of development which makes it useful to report on them at this time.
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FIGURE 3
CONSTANT CURRENT SOURCE
LEGEND - FIGURE 3

B-1 Battery, 22.5 Volt
B-2 Battery, 90 Volt
B-2 Busser
C-1, C-2 Condenser, 20 microfarad, 480 Volt
I Lamp G.E. #44, Holder Dialco 91408
J-1 Input Resistance Jack
J-2 Calibration Resistance Jack
J-3 Output Jack
K Relay, 15,000 ohm coil DPOT, Simplytrol 1816-15
M Panel Meter 0-25 ma, lowlimit, contacts, Simplytrol Model #241
(Assembly Products Co., Chagrin Falls, Ohio)
R1 Coarse Input resistance, 10,000 ohm, wire wound
R2 Fine Input resistance, 1,000 ohm, wire wound
R3 Resistor, 100,000 ohm 2 watt
R4 Resistor, 15,000 ohm 10 watt
R5 Resistor, 500,000 ohm 1 watt
R6 Resistor 4,700 ohm 1 watt
R7 Resistor 15,000 ohm 1 watt
R8 Resistor 50,000 ohm 1 watt
R9 Resistor 150,000 ohm 1 watt
R10 Resistor 10,000 ohm 1 watt
S1 Switch, Range Selector
S2 Switch, Output
S3 Switch, reset (normally closed)
FIGURE 7
TRIGGER OUTPUT RELAY CIRCUIT