March 5, 1940. G. F. SMITH 2,192,777

CATHODE RAY TUBE TITRATION APPARATUS

Filed Nov. 27, 1936 3 Sheets-Sheet 1

Fig. 1.

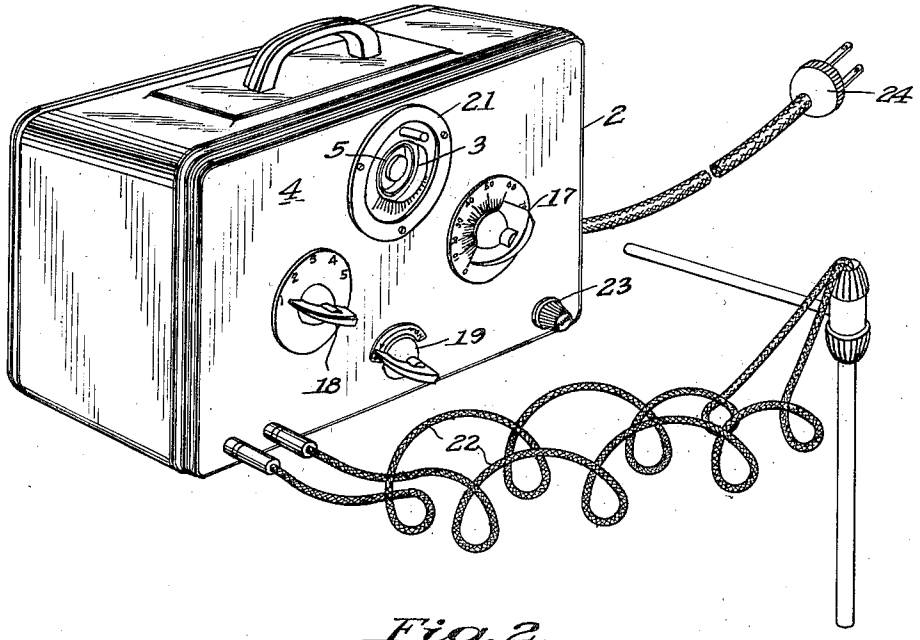
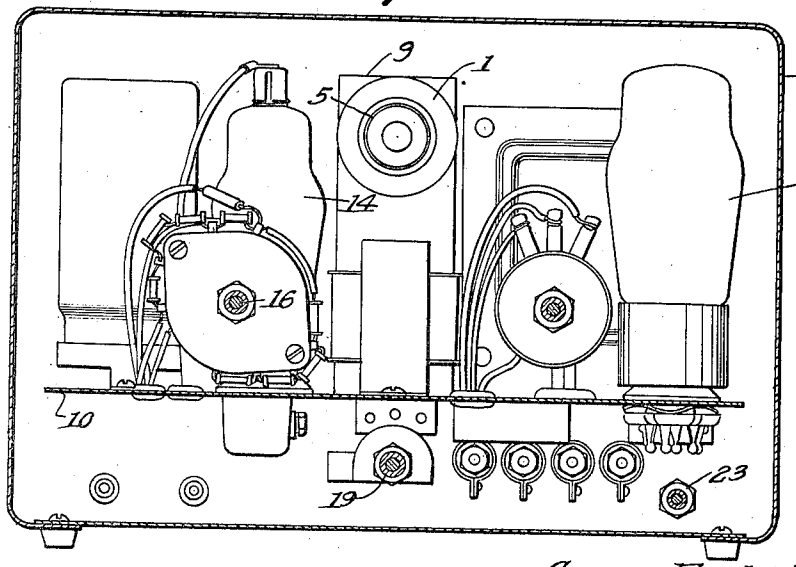


Fig. 2.



Inventor

George Frederick Smith

By W. J. M. Powell

Attorney

March 5, 1940. G. F. SMITH 2,192,777

CATHODE RAY TUBE TITRATION APPARATUS

Filed Nov. 27, 1936 3 Sheets-Sheet 2

Fig. 3.

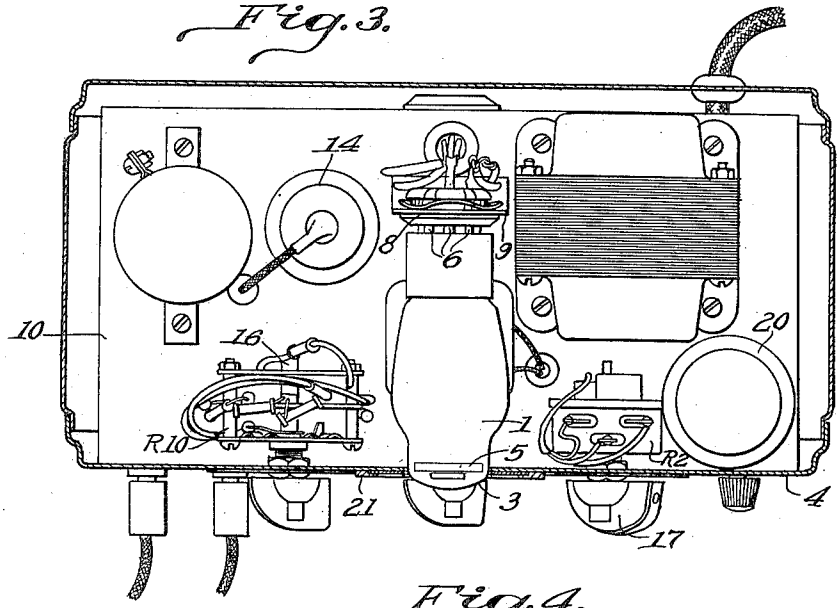


Fig. 4.

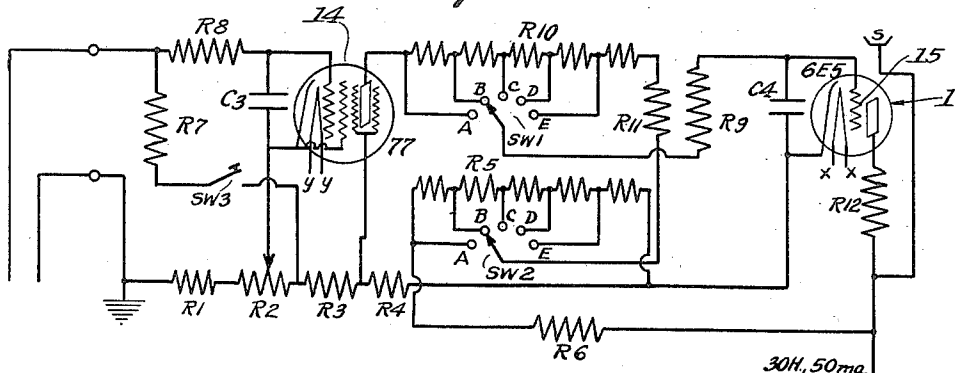
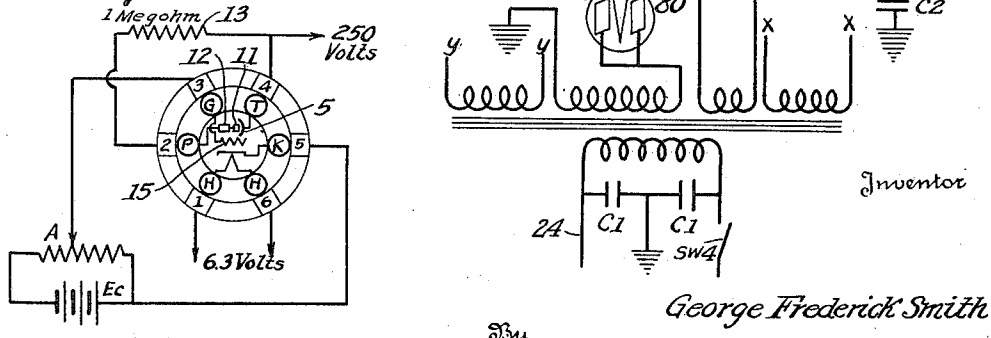


Fig. 5.



Inventor

George Frederick Smith

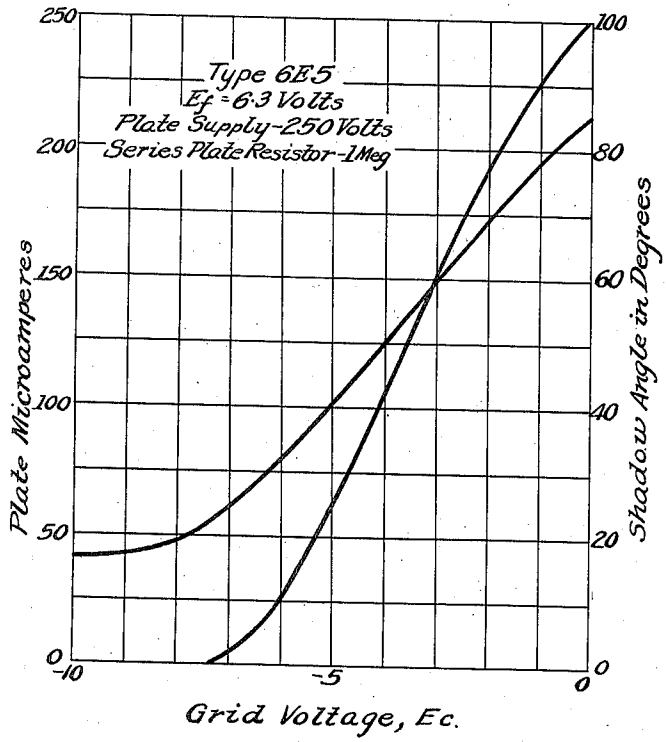
By W. S. McDowell Attorney

March 5, 1940. G. F. SMITH 2,192,777

CATHODE RAY TUBE TITRATION APPARATUS

Filed Nov. 27, 1936 3 Sheets-Sheet 3

Fig. 6.



Inventor
George Frederick Smith

By W. J. M. Howell
Attorney

Patented Mar. 5, 1940

2,192,777

UNITED STATES PATENT OFFICE

2,192,777

CATHODE RAY TUBE TITRATION APPARATUS

George Frederick Smith, Urbana, Ill., assignor to The G. Frederick Smith Chemical Company, Columbus, Ohio, a corporation of Ohio

Application November 27, 1936, Serial No. 113,048

2 Claims. (Cl. 175—183)

This invention relates to potentiometric titration apparatus of the type utilizing electronics in the actuation thereof. Application of the vacuum tube or triode to the field of electrometric titrations has resulted in the simplification of such apparatus in that the progress of the titration can be followed continuously and automatically and without the employment of a potentiometer used in earlier electro-titration apparatus. Such electronic titrimeters may be used advantageously in the broad field of controlling and noting various chemical reactions as precipitation, neutralization and oxidation-reduction.

Electronic tubes have been used in such apparatus for some time and have now reached a point of development where the same may be connected with and operated by standard commercial electrical circuits, dispensing with the use of batteries or current developing cells. However, the most advanced electro-titrimeters employ in conjunction with the electronic tube amplification sensitive and relatively expensive micro-ammeters, and it is the object of the present invention to further improve such electro-titrimeters by the elimination of the micro-ammeter, utilizing in lieu thereof a cathode ray tube as the indicator.

Among other objects of the invention are: the provision of an electronic-titrimeter of the direct reading line-operated type in which an expensive and easily injured micro-ammeter is not required; the provision of a titrimeter wherein the complete apparatus assembly is self contained, sturdy and readily portable, having a total cost which slightly exceeds that of the micro-ammeter hitherto employed in all line-operated thermionic titrimeters; the provision of titrimeter apparatus so constructed as to possess a high degree of resistance against injury due to accidental or faulty manipulation; the provision of a titrimeter which can be used in connection with either (*a*) the mono-metallic, externally polarized electrode system or (*b*) the bi-metallic self-polarizing system, or (*c*) the usual half cell and reference electrode system; the provision of a titrimeter of the character desired wherein the sensitivity of the potential change indicating mechanism is far greater than the usual electron tube amplification arrangement as applied to the conventional micro-ammeter of a continuous indicator system, whereby through said increased sensitivity not only is one able to determine continuously the progress of the reaction under determination but also to gain a definite indication of the reaction velocity; a titrimeter wherein analytical reactions with potential breaks at the equivalence points of the order of magnitude of 50 millivolts can be readily followed, the latter being the lower limit of present working practice, and without involving the necessity at such lower limits for mathematical analysis of the data obtained; an electronic type of meter wherein a sufficiently linear relationship exists between applied E. M. F. and the cathode ray tube's sector shadow effects to readily follow the titration; in the provision of an improved indicator for titrimeters wherein no moving parts are involved and wherein instantaneous response of the indicator to applied impulses is obtained and immediately readily discernible, and other features of operation, construction and arrangement which will be in part obvious or pointed out hereinafter.

For a further understanding of the invention, reference is to be had to the following description and the accompanying drawings, wherein:

Fig. 1 is a perspective view of the cabinet in which the apparatus comprising the present invention is contained;

Fig. 2 is a vertical sectional view taken through the cabinet and disclosing the interior apparatus;

Fig. 3 is a horizontal sectional view of the cabinet, with the apparatus therein disclosed in plan;

Fig. 4 is a diagrammatic view of the several circuits utilized by the present invention;

Fig. 5 is a similar view of the cathode tube.

Fig. 6 is a diagrammatic view disclosing a graph illustrating variation in shadow angles and plate current at different bias voltages of a cathode ray tube.

Among the recent developments in electronic tube manufacture is the so-called cathode ray tube, which has been quite widely used as the visual timing indicator in modern radio receiving sets. Commercially the tube is known as the 6E5 or the "magic eye" tube. This unique tube, actually two tubes in one, consists of a triode section or amplifier, in the top of which is mounted a miniature cathode ray tube. A concave disk electrode near the top of the tube, designated the fluorescent screen or target, glows as a green fluorescent circular area when the tube is in operation. The cathode, common to both tube sections, extends into and above the target and terminates in a black button-like shield in the top of the tube. In such a tube, the electron beam is produced and controlled as follows: With the cathode heated, and 200 to 300 volts applied to the concave disk electrode or

target, a screen of electrons from the cathode bombards the target electrode causing the fluorescent screen to glow with a greenish coloration. A ray controlling electrode or deflecting plate is connected to the plate of the triode section of the tube and extends through and into the confines of the target electrode. The ray controlling electrode or deflecting plate is mounted very close to the cathode and is thus interposed in the beam of electrons streaming to the target. Depending upon its potential, the ray controlled electrode or deflecting plate serves to deflect the electron streams from their original paths. This deflection is made evident by the appearance of a sector of shadow on the fluorescent target, there being no electrons in the restricted beam or beams to cause fluorescence.

Since the ray controlling electrode or deflecting plate is connected directly to the triode plate, its potential varies directly with it. With decrease in negative grid bias, the triode plate current increases, increasing the voltage drop in the resistance R_{12} (see Fig. 4), thus lowering the potential of the ray controlling electrode. With this condition, there is a maximum deflection of the electrons appearing on the target as a maximum shadow. The angle of the shadow varies from 90° to 100° at zero bias, to 0° at negative 8.5 volts bias applied to a triode grid of the cathode ray tube.

This combination of the triode and cathode ray tube becomes essentially a self-contained vacuum tube voltmeter in which the cathode ray tube replaces the expensive micro-ammeter ordinarily used in apparatus of this character. The versatility and adaptation of such a combination are at once apparent, particularly in view of the rapid response to applied E. M. F., because there are no mechanically moving parts as in prior devices.

The cathode ray tube, indicated at 1 in the accompanying drawings, is disposed in a horizontal position within the interior upper portion of a cabinet 2 with the other end of the glass shell 3 of the tube projecting through an opening in the removable front panel 4 of the cabinet so that the fluorescent target 5 of the cathode 2 may be viewed from the front of the cabinet. The contact prongs 6, which project from the base 7 of the tube, are received within a socket member 8 carried by a stationary bracket 9 projecting upwardly and vertically from a horizontally disposed supporting shelf 10 which is stationarily connected with the front panel 4 of the cabinet and is adapted to support the apparatus contained within said casing, so that upon removal of the front panel from the casing, all interior apparatus will be readily accessible.

A cathode ray tube, such as indicated at 1, is a standard commercial product and therefore an extended and detailed description of its construction and operation need not be given herein. However, to facilitate a clear understanding of the present invention, the following brief description regarding the construction and operation of such a tube is offered.

By referring to the schematic diagram shown in Fig. 5, a clear understanding may be obtained as to the action taking place when a cathode ray tube is used in circuit applications. It will be assumed that the circuit Ec is variable by means of the control A. If 250 volts are applied to the target 5, electrons will be attracted to it and will cause its fluorescent glow. The deflecting plate or ray control electrode 11 is connected to the triode plate 12 as indicated in the diagram. These two elements are connected to the target electrode 5 through a 1 megohm resistor indicated at 13. If zero bias be now applied to the triode section of the tube, the maximum plate current will flow to the triode plate. This current flows through the resistor 13 and thereby produces a voltage drop between the target 5 and the deflecting plate 11.

Since the plate is negative with respect to the target, it will reduce the number of electrons reaching the target. Because of the shape and location of the deflecting plate, a shadow will be cast around the target. The shadow angle will be about 100°. If the bias is increased slightly to approximately two volts, the plate current will decrease somewhat, decreasing the voltage difference between the target and the deflecting plate, resulting in the shadow angle closing in since not as many electrons are repelled as before. After two volts bias is applied, the shadow angle change per volt bias applied to the grid increases somewhat and remains constant until about six volts bias is applied. From six to eight volts, the rate of change slows up somewhat but at eight volts, the shadow has usually entirely disappeared.

In Fig. 6, there has been shown a graph which illustrates how the shadow angles and the plate current of the triode vary if different bias voltages are applied to the triode section.

A schematic diagram of the circuit employed by the present invention in which the cathode ray tube indicator is utilized, is shown in Fig. 4. The design of the circuit and the arrangement thereof represent a compromise between sensitivity, stability and linearity of response, together with the use of A. C. line power. The present circuit has been laid out with particular reference to oxidation-reduction titrations using the bimetallic system, with potential breaks of 100 to 200 millivolts. Since a change of about 8.5 volts is required to completely operate the shutter or indicator, as above pointed out, a voltage amplification of 100 is necessary. This has been realized by the use of a voltage amplifying vacuum tube 14, with the output of this tube operating the cathode ray tube 1. The tube 14 is known commercially as a 77 high mu pentode tube. A variable sensitivity controlled rheostat R_{10} is employed to control the output of the tube 14 in order that the break in applied E. M. F. suffices to operate the shadow. The rheostat or resistor R_{10} serves to positively bias the triode grid 15 of the tube 1 and, therefore, it is necessary to balance out this potential by an opposite potential developed across the resistance or rheostat R_5. In order to realize maximum simplicity in adjustment, the resistances R_5 and R_{10} have been grouped and are controlled from a single operating shaft, indicated at 16. There are five tapped positions providing five adjustments in sensitivity and allowing a full 90° movement of the shadow for applied E. M. F. breaks varying between 100 and 300 millivolts. Under these conditions, the cathode ray tube is maintained in an essentially sensitive condition irrespective of the sensitivity setting.

An additional manually operated indicator control R_2 is used to balance out the initial potential developed by the titrating cell and bring the indicator shadow to an initial setting at the start of a titration. The operating knob of the

resistor R_2 is indicated at 17 in Fig. 1 of the drawings, while the corresponding knob for the resistances R_5 and R_{10} is indicated at 18. These two manual controls take care of all necessary adjustments of the "shadow" and "breaks" in applied E. M. F. Under these conditions, the position of the shadow of the tube 1 is at all times controlled by the net bias of the amplifier tube 14 which is maintained at the same value at the center of all titrations regardless of the potential developed across the titrating cell. An essentially constant sensitivity is thus realized over any reasonable range of initial potentials.

Provisions are also made for use of the apparatus with an externally polarized mono-metallic (Pt.-Pt.) electrode system. A polarizing current of approximately 1.5×10^{-5} amperes is bled from the resistances R_1 and R_2 by shunting the latter directly across the titrating cell 18 through a 300,000 ohm resistor R_7. This method of obtaining the polarizing current is entirely practical as the internal resistance of the titrating cell is negligible in comparison with the resistor R_7, so that the operating bias on the amplifier tube 14 is only slightly affected. A manual controlling switch for this circuit is indicated at 19, this switch being of any conventional on and off type.

The 500 volts of direct current supply is obtained from the vacuum tube indicated at 20. This tube commercially is known as the 80 type and is connected as a half wave rectifier with which adequate filter and bleeder resistors furnish all grid, screen and plate voltages. It should be noted that the cathode of the cathode ray tube 1 operates preferably at 200 to 300 volts to ground and that a separate heater winding must be used.

In actual use, the above circuit is sufficiently stable for all potentiometric titrations. For that reason, increased stability obtained by application of a bridge or mu-balanced principle has not been deemed necessary, especially as equilibrium voltages are not required. Line fluctuations of five volts introduce enough variation to operate the shadow of the cathode tube. Such an extreme variation during a titration may for all practical purposes be considered remote. A gradual drift of the shadow, especially during the warming up interval following the initial heating of the tubes may be noted; random fluctuations, however, are scarcely discernible. The sensitivity is such that most practical titrations using the bi-metallic system will cause a significant movement of the shadow generally a full 90°. In other words, for maximum sensitivity, a change in applied E. M. F. of 100 millivolts will cause a full 90° change. Angular displacements of 10 to 20° can be noted readily, so that end-point changes considerably less than 100 millivolts are satisfactory.

The cathode ray tube 1 is preferably mounted at the top-center of the front panel 4 of the cabinet and the fluorescent screen of this tube with the wedge shaped, non-fluorescent sector during operation, is found in the center of the lower semi-circular portion of the exposed end of the tube. A circular metal frame 21 rotatably adjustable about the longitudinal axis of the exposed end of the tube 1 can be provided with a scale of 90° range with 5° intervals to correspond to the various degrees of opening of the wedge-shaped non-fluorescent area of the cathode ray tube. Its calibrations should be made after the ray tube is mounted and affords a convenient means for noting the variations in the sector shadow. The control knobs and their associated dials for the resistances R_5, R_{10} and R_2 are mounted at either side of the middle portion of the panel below the exposed end of the cathode ray tube and spaced substantially equi-distantly from the latter.

The left hand dial or knob, when viewed as in Fig. 1, controls the sensitivity of the cathode ray tube to applied E. M. F. At setting 1 of this dial, the non-fluorescent screen sector can be increased from 0 to 90° with an applied E. M. F. of 100 millivolts. Since unmistakable equivalence point sector displacements of 45° are entirely satisfactory, end point breaks of 50 millivolts are ample in citing potential changes. At a setting of 5 for sensitivity control, the same sector displacements of the cathode ray tube require 300 millivolts. Since this is approximately the maximum equivalence point "break" for titrations of reductants of low oxidation potential by oxidants of high oxidation potential, the range covered is ample and could be further increased if desired. These values were substantiated using a standardized potentiometer circuit and the relationships were shown to be sensibly linear over the entire working range of the sensitivity control.

The right hand dial control, when the apparatus is viewed as in Fig. 1, employed for governing the resistance R_2, operates the setting of the initial reading of the non-fluorescent wedge sector at the beginning of a titrational operation. In case a particular titration proceeds to the equivalence point with an appreciable change in potential, this dial setting may be changed during the progress of the titration. This scale setting is of value in checking the duplication of starting and final potentials.

The center switch 19 in the lower central part of the panel 4 is the "off" and "on" switch of the polarizing circuit. The electrode connections for the titrating cell 18 are shown in the lower left side of the panel, when viewed as in Fig. 1 and extension cords 22 unite the same with the titration cell. The operation of the variable tube sector from closed to open and vice versa is provided by changing positions of these electrodes. Using a polarized mono-metallic system, the sector operates only in one direction, from open to closed.

The circuit is fused as at 23, and as shown in the lower right hand corner of the panel as when viewed in Fig. 1, the fuse being replaceable from the front. A 110 A. C. power line connecting plug 24 is connected with the apparatus and the switch of this power circuit is made a part of the sector setting dial control. The fluorescence of the cathode ray tube gives excellent contrast with the non-fluorescence sector space in artificial light and in direct daylight of ordinary intensity. Lecture demonstration using the cathode ray tube may be facilitated by employing a flexible cable to connect and separate cathode ray tube to the apparatus assembly, so that the cathode ray tube may be disposed remotely with respect to the cabinet apparatus.

From the foregoing, the practical advantages to be derived from the use of the present invention will be apparent, it is believed, to those skilled in the use of apparatus of this type. The practical results from the elimination of the milla-ammeter used in the previously described electronically operated potentiometric equipment are at once apparent. With one unit of equipment, the present invention makes available a titrimeter which applies the cathode ray tube to substitute for the use of the milla-ammeter of other continuous recording titrimeters which can be powered by a single 110 volt A. C. line source. The

apparatus comprising the present invention can be used with any previously employed electrode system. The calomel or silver chloride electrode and platinum electrode may be used. The monometallic (Pt.-Pt.) electrode system using the polarizing current control afforded by the present invention is operative with equal facility. The much to be preferred Pt.-W self-polarizing electrode system is ideal.

The advantage in the use of the present invention is most apparent, due to the instantaneous response of the cathode ray tube sector shadow to changes in potential in the titration cell. This has the double advantage that the warning of the approach to the equivalence point during titration is greater than would be possible through using a continuous reading milla-ammeter with its moving parts and which are inherently sluggish in responding to applied impulses. In the same manner, the velocity reaction in titrating cell is at once apparent. A reaction which is too slow, due to incorrect acidity, temperature, etc., is readily noted and proper adjustment can be made. For the same reasons, a color indicator end point determination is not as satisfactory. The warning of the approach to the end point is not nearly as good and almost no indication of the rapidity of the reaction is afforded with a color type of indicator. Again, all oxidation-reduction indicators are not reversible which is not true of the end point determination afforded by the present invention.

If it is desired to read the actual potential of the titrating cell throughout the progress of the titration, such a working potential at any time may be conveniently determined by the use of a simple potentiometer with direct reading scale, supplied as an accessory. The use of an extension cable and auxiliary cathode ray tube enables one, by placing it alongside of the titration beaker, to observe the effects of the dropwise circuit of reactants without glancing from the titration beaker to the cabinet assembly. The effect is the same as that obtained when using a conventional color indicator.

The present invention may be used advantageously as a part of the equipment of research and routine analytical laboratories as well as in instructional or educational institutions interested in the teaching of instrumental methods of analysis.

What is claimed is:

1. In electronic titration apparatus, means for measuring the voltage of a titrating cell circuit having a pair of electrodes, an amplifying circuit for connection with said cell circuit comprising a pentode electronic tube amplifier having an input circuit and an output circuit, variable resistance means connected in the input circuit of said amplifying circuit for series connection with said electrodes, variable resistance means in the output circuit of said pentode tube amplifier, a cathode ray electronic tube coupled with said amplifying circuit comprising an electron emitting cathode, a plate, a control grid, and a fluorescent target, said resistance means in the output circuit of the amplifying tube variably biasing the grid of said cathode ray tube, and additional variable resistance means between said pentode amplifying tube and cathode ray tube adapted to be adjusted conjointly with the variable resistance in the output circuit of the pentode amplifier for adjusting the sensitivity of the cathode ray tube for different conditions in said input circuit to give a substantially constant range of indication on said fluorescent target.

2. In electronic titration apparatus, means for measuring the voltage of a titrating cell circuit, an amplifying circuit for connection with said cell circuit comprising a thermionic amplifier having an input circuit and an output circuit, variable resistance means connected in the input circuit of said amplifying circuit, variable resistance means in the output circuit of said titrating amplifier, a cathode ray electronic tube coupled with said amplifying circuit comprising a control grid and a fluorescent target, said resistance means in the output circuit tube of the thermionic amplifier variably biasing the grid of said cathode ray tube in accordance with varying conditions in said titrating cell circuit, and additional variable resistance means between said thermionic amplifier and cathode ray tube adapted to be adjusted conjointly with the variable resistance in the output circuit of the titrating amplifier for adjusting the sensitivity of the cathode ray tube for different conditions in said input circuit to give a substantially constant range of indication on said fluorescent target, said first-mentioned variable resistance means in the input circuit of said thermionic amplifier serving to balance out the initial potential developed by the titrating cell and to bring the indicator shadow on the fluorescent target to an initial setting at the start of titration.

GEORGE FREDERICK SMITH.