

## SCIENTIFIC SECTION

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### CONTINUOUS-READING TITRATION APPARATUS.\*

BY LAWRENCE H. BALDINGER.<sup>1</sup>

As an aid in presenting the subject of electrometric titration to a class in Analytical Pharmacy, a simple, inexpensive apparatus was constructed which was rugged enough to withstand frequent use by students, sufficiently accurate to emphasize continuous-reading electrometric titration methods. The apparatus as described can be assembled and wired in about three hours. All of the parts of the apparatus except the galvanometer and the milliammeter can be purchased from a radio dealer. The total cost should not exceed twenty-five dollars.

*Discussion.*—The ordinary potentiometric titrations involve the reading and plotting of E. M. F. values of the titration cell *versus* the milliliters of reagent used.

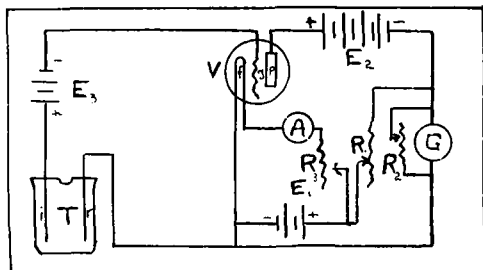


Fig. 1.—Continuous-reading titration apparatus.—V, electron tube; f, filament; p, plate; g, grid; T, titration cell; i, platinum indicator electrode; r, reference electrode; G, galvanometer; A, milliammeter; R<sub>1</sub>, 25,000 ohm rheostat; R<sub>2</sub>, 25 ohm rheostat; R<sub>3</sub>, 85 ohm rheostat; E<sub>1</sub>, 3-volt battery; E<sub>2</sub>, 22.5-volt battery; E<sub>3</sub>, 1.5-4.5-volt battery.

Using the vacuum-tube apparatus no plotting is necessary unless desired for laboratory records. Instead of using a "balanced" circuit, *i. e.*, a circuit in which the E. M. F. of the titration cell is balanced against a known E. M. F., the vacuum-tube apparatus employs an "unbalanced" circuit in which the course of the reaction is followed by observing galvanometer deflections. The theory upon which this apparatus is based, as well as a description of the newer wiring diagrams and uses, has been discussed in the literature (1). Inasmuch as some difficulty was experienced in duplicating results using some previously reported wiring diagrams, the apparatus used in this work was finally assembled according to the method of Goode (*loc. cit.*). See Fig. 1.

In addition to the ease with which the course of a reaction can be followed by observing the galvanometer deflections, this type of apparatus offers the advantage over the potentiometric method of titration in that the vacuum tube operates as a voltmeter which draws practically no current from the titration cell.

The heated filament (f) emits a stream of electrons which impinge upon the plate (p) setting up a current which activates the galvanometer (G). The current in the galvanometer circuit is made up of two parts: (a) the residual plate current, and (b) that current which is a function of the grid bias developed by the electrodes of the titration cell. As the grid bias is changed the plate current is altered correspondingly depending upon the amplification factor of the vacuum tube. The residual plate current is so large in comparison with the current which is a function of the

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grid bias that it must be balanced by an equal and opposite current before a titration can be performed. An RCA Radiotron tube, type UX-199, drawing 0.04–0.05 ampere current at optimum operation, was used in this apparatus. A plate voltage of 22.5 volts was found to be sufficient for our work. Although additional grid bias was not needed in our experiments, C-battery terminals were provided on the panel. A 25-ohm variable resistance ( $R_2$ ) acts as a galvanometer shunt. The current of the filament battery acting through a 25000-ohm variable resistance ( $R_1$ ) serves to balance out the residual plate current and thereby to increase the sensitivity of the galvanometer. The D'Arsonval galvanometer<sup>1</sup> (G) is an inexpensive model having a resistance of 150 ohms and a sensitivity of 1.7 megohms at 12.5 cm. The milliammeter (A) may be either a portable or panel type. See Figs. 1 and 2.

In order to simplify still further the apparatus used, graphite and platinum, tungsten and platinum, and silicon carbide-platinum electrode pairs were used in place of the calomel half-cell-platinum assembly as proposed by previous workers. Inasmuch as only E. M. F. changes, not actual values, are observed with this apparatus, nothing is to be gained by the use of the calomel half-cell, provided that other electrodes will give consistent results. Brünnich (2) has employed the graphite and platinum electrode pair in neutralization reactions, connecting the electrodes directly to a galvanometer through a tapping key. Depolarization of the electrodes, an obvious result of prolonged key contact in Brünnich's assembly, is eliminated by the use of the vacuum-tube voltmeter. Furman and Wilson (3) have extended the use of the tungsten-platinum electrodes to oxidation-reduction titrations in a system analogous to that of Brünnich. Kamienski (4) showed that silicon carbide is an ideal substance to use as a constant reference electrode since its potential is almost independent of the chemical properties of the solution in which it may be immersed. The electrode systems were constructed in compact units in order to minimize breakage. See Figs. 2 and 3.

For the titration of strong acid with strong base, weak acid with strong base, and iodine with sodium thiosulphate, it was found that the graphite and platinum electrode pair gave satisfactory results. Both the tungsten-platinum assembly and the silicon carbide-platinum electrodes gave good results in the titration of ferrous ammonium sulphate with potassium dichromate solution. In all experiments the electrometric titrations were checked using standard methods of analysis. The galvanometer deflections were plotted *versus* milliliters of reagent and curves were drawn through the points to show the course of the reaction. See Fig. 4. In order to show the practicability of this apparatus in a course in Analytical Pharmacy, a number of ferrous iron preparations of the U. S. P. were analyzed, using the tungsten-platinum and the silicon carbide-platinum assemblies. Simultaneously with the use of the vacuum-tube apparatus, the titrations were checked, using diphenylamine

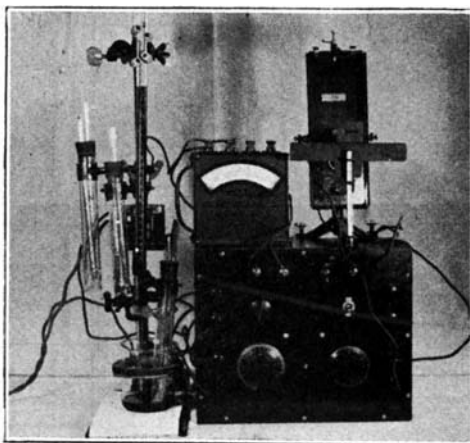


Fig. 2.—Titration apparatus.

<sup>1</sup> Central Scientific Co., Chicago, Ill. Catalog No. F-4451.

as an indicator. In practically all of the titrations of these compounds, it was found that about 0.15 ml. more of potassium dichromate solution was necessary to reach a diphenylamine end-point after the end-point had been indicated by the apparatus. This is in agreement with the findings of Knop (5) and of Kolthoff and Sarver (6) who have suggested a correction factor for the oxidation of diphenylamine.

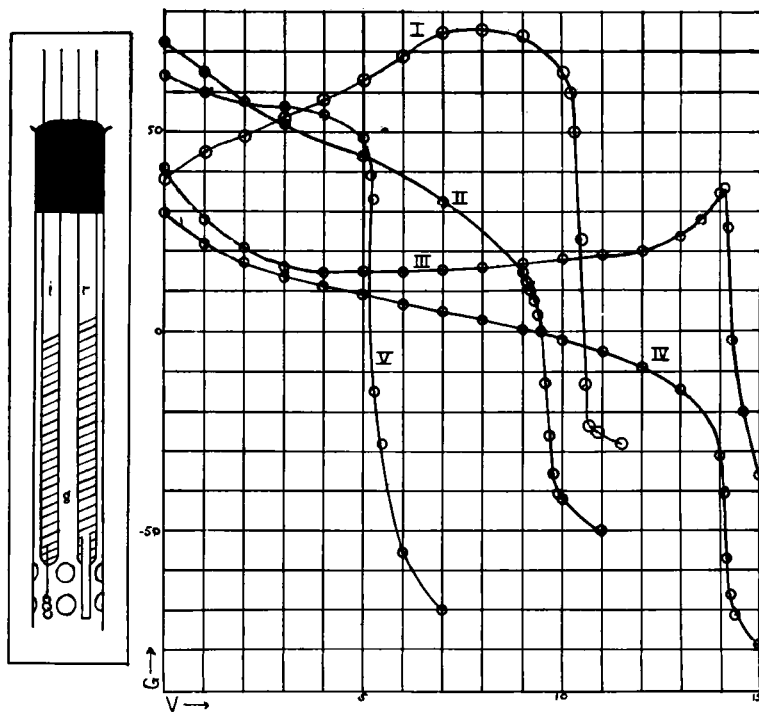


Fig. 3.— Electrode assembly: i, platinum electrode; r, reference electrode; g, glass tubing. Fig. 4.—Titration Curves.—G, galvanometer readings; V, millimeters of reagent; I, hydrochloric acid with sodium hydroxide. Graphite-platinum electrodes. II, acetic acid with sodium hydroxide. Graphite-platinum electrodes. III, Mohr's salt with potassium dichromate. Tungsten-platinum electrodes. IV, Mohr's salt with potassium dichromate. Silicon carbide-platinum electrodes. V, Iodine with sodium thiosulphate. Graphite-platinum electrodes.

*Procedure.*—A weighed sample is treated according to quantitative methods up to the titration stage. In the case of the ferrous compounds the sample is treated with 20 ml. of diluted sulphuric acid (1 volume sulphuric acid with 4 volumes of water) and 15 ml. of a sulphuric-phosphoric acid mixture (75 ml. sulphuric acid and 75 ml. phosphoric acid diluted with water to 500 ml.). Following this treatment the iron solution is diluted to 200 ml. with water. After immersing the electrodes in the solution the filament current is increased to 0.05 amperes and the galvanometer adjusted to obtain a deflection of 50 or 60 mm. For best results the galvanometer shunt should be completely eliminated before beginning the titration. Resistance  $R_2$  should be used only to protect the galvanometer from sudden current changes while adjusting resistance  $R_1$ . After some practice the experimenter will have little trouble in obtaining the proper galvanometer reading prior to titration. The reagent is run into the titration cell, at first, several milliliters at a time, and then more slowly, as the equivalence point is reached, when galvanometer readings are taken

more frequently. During some titrations it may be necessary to readjust the galvanometer by means of resistance  $R_1$ , especially if an instrument with a small scale is used. Vigorous stirring of the reaction mixture is necessary and is best accomplished by a small motor stirrer. It is well to wait thirty seconds after each addition of reagent to allow the galvanometer reading to become constant. The end-point is characterized by a sudden large deflection, *i. e.*,  $dE/dV$ , the rate of change of the E. M. F. of the titration cell with a small change in concentration of the reagent, approaches a maximum. It was observed that concordant results could be obtained when using the graphite or silicon carbide electrodes if, after each titration, the electrodes were immersed in cleaning solution, followed by thorough washing with distilled water. This apparatus is being used at the present time in these laboratories for the titration of alkaloids. A report of the work will appear shortly.

#### SUMMARY.

1. The use of graphite-platinum, tungsten-platinum and silicon carbide-platinum electrode pairs with a vacuum-tube titration apparatus has been suggested and illustrated.
2. The apparatus has been applied to the titration of some ferrous iron compounds of the U. S. P.

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- (3) Furman and Wilson, *J. Am. Chem. Soc.*, 50 (1928), 277.
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- (6) Kolthoff and Sarver, *J. Am. Chem. Soc.*, 32 (1910), 539; 52 (1930), 4179; 53 (1931), 2906.

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## A NOTE ON THE ASSAY OF REDUCED IRON.\*<sup>1</sup>

BY MARGARETHE OAKLEY AND JOHN C. KRANTZ, JR.

#### INTRODUCTION.

Reduced iron has found a place in practically all of the pharmacopœias of the world. In some, the evaluation is expressed in terms of metallic iron and in others, the total iron content is employed. Winter (1) reviewed these various standards in 1913. The eighth revision of the United States Pharmacopœia employed the iodimetric process of assay. The ninth and tenth revisions employed the well-known mercuric chloride method. The British Pharmacopœia specifies the copper sulphate procedure; this method depends upon the displacement of the copper by the iron. In all of these methods, the ferrous or ferric oxide present in reduced iron remains unattacked by the reagents employed. In 1909 Frerichs (2) reviewed

\* Scientific Section, A. P. H. A., Washington meeting, 1934.

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