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CONSTANT CURRENT SOURCE FOR AUTOMATIC
COULOMETRIC TITRATIONS

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Summary

A simple, but versatile constant current source for automatic coulometric titrations is described. The unit is suitable for use with a commercial automatic pH titrimeter and will accommodate wide variations of mains voltage and load resistance.

Coulometric titrations may be carried out "fast" or "slow" with a choice of four current ranges (2-37 mA) for titrations up to or near the end point. A slow "1 mA" range is available for approaching the end point and the titration of microgram amounts of material. The automatic pH titrimeter provides for automatic change from fast to slow generation of the reagent and for stopping the titration at the selected end point.

The utility of the equipment has been demonstrated by the estimation of chromium with electrogenerated ferrous iron. The unit should be suitable for many other coulometric titrations.

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1. INTRODUCTION

The basic principles of coulometric analysis were first formulated by Szebedelly and Somogyi⁽¹⁾ in 1938. In recent years, this important method has received increasing attention because of its ease of interpretation and inherent precision. The subject has been extensively reviewed.^{(2), (3), (4), (5).}

Two methods of carrying out coulometric titrations are widely used. In the first, the current is allowed to vary and the total quantity of electricity determined by integration. This integration may be performed chemically⁽⁶⁾ or electrically and Smythe⁽⁷⁾ has described an integrated-current source suitable for automatic titrations.

The second widely used approach is to maintain the current constant and measure the time required to arrive at the end point. Many of the circuits described to maintain currents constant lack flexibility, are not suitable for automatic operation, and are expensive.

The versatile constant current source described in this report is relatively inexpensive, and is suitable for automatic operation. Because of the large quantity of electricity (96,522 coulomb⁽⁸⁾), associated with a gram-equivalent, the coulometric method is particularly suited for the determination of quantities of materials in the 20 mg to microgram range. Larger quantities of material may frequently be determined more conveniently by conventional means. Currents from 40 to 1 mA are those most usually used⁽²⁾ in this work.

To be suitable for automatic operation, the constant current source should be capable of being used in conjunction with an automatic pH titrimeter and should operate satisfactorily for varying mains voltage and cell resistance.

2. DETAILS OF CONSTANT CURRENT SOURCE

The constant current source for automatic coulometric titrations provides the following facilities:-

- (i) Five constant current ranges are provided; 1.13, 2.60, 6.80, 16.8 and 36.5 ma. These values are set by the series resistors chosen which, in this case, are commercial wire-wound resistors run at about 1/10 of their rated dissipation. Any two of these ranges may be chosen as "fast" and "slow" ranges by means of switches.
- (ii) Relays are included which can be operated by the "fast" and "slow" indications from a commercial automatic pH titrimeter. These relays cause the two selected currents to be delivered to the cell in turn and register the time on each range on appropriate registers. The "slow" range may of course, be used for manual titration of sub-microgram quantities of the constituent.
- (iii) A simple inexpensive, timing unit is incorporated in the apparatus, the mains frequency being used as the reference. In cases where the stability of the mains frequency is inadequate, provision is made for the addition of an external timing unit. This unit is under development.

Figure 1 shows the principle of the constant current source. The current through the load is passed through a standard resistance R_1 . The voltage developed across R_1 is compared with a reference voltage, the difference amplified in an amplifier of gain G and used to control the current flowing through a series valve.

For this arrangement, it may be shown that the incremental output impedance at the cell terminals, Z_o , is approximately equal to $G.R_1$. Now, if a 40 mA current is to be held constant to 0.1% for a 500 ohm change in load, then it is required that

$$Z_o = 500,000$$

The most convenient reference voltage is an 85V gas regulator tube. Then, for the 40 mA current, $R_1 = 2000$ ohm approximately, and it is required that $G = 250$.

For lower values of current R_1 is proportionately larger and the output impedance proportionately higher making the stability against changes in cell resistance much better.

The situation with regard to voltage stability is rather different. If (de_p) is the voltage change at the plate of the series valve and (de_o) the change across the load, then it may be shown that

$$\frac{de_o}{de_p} = \frac{1}{\mu \cdot G} \text{ (approximately)}$$

where the μ is the amplification factor of the series valve. The μ of the triode-connected CV2127 is about 4 at low currents and increases with increasing current. Thus, the stability for changes in mains voltage will increase as the load current increases unlike the stability for changes in load resistance which is greatest at lower currents. In practice the most troublesome result of fluctuations in the mains input voltage will be changes in the reference voltage supplied from the gas tube regulator and changes in the heater voltage of the amplifying valves.

The required gain of 250 from the D.C. amplifier could not be obtained easily from a single CV4014 (EF91). In order to improve the situation a triode is used as the anode load of the pentode. By this means, a gain of 250 is readily achieved.

For the reference voltage source, an 85A2 gas diode is the most convenient choice. When drawing approximately 4-1/2 ma the 85A2 has a stability of .1% which is satisfactory. However, the output voltage changes by 1/2% for each 1 ma change in current. Thus, if the 85A2 were fed from a 150V source through a 15K resistor (to give 4-1/2ma operating current), then to restrict the changes in this current to .2ma, (which is required in order to restrict the changes in output voltage to .1%); it would be necessary to keep the voltage input to $150 \pm 3V$. This necessitates using a second 150V regulator on this line.

3. DESIGN OF TIMING CIRCUIT

The standard time source is the 50 c/s mains. The short term stability of the mains frequency in Sydney is usually of the order of .1%, but deviations of as much as $\pm 1\%$ may occur (9). This was checked by taking several 100 sec. counts on a scaler with a stop-watch.

The 50 c/s mains is counted down to 5 c/s with a simple CV2271 Dekatron circuit and this 5 c/s signal is used to drive PMG registers. The Dekatron gives out a positive pulse 20V in amplitude and 10 ms. in length. This is stretched to 100 ms. in a monostable multi-vibrator and used to drive a cut-off pentode into conduction. Driving PMG registers at 5 c/s from valve circuits appears to demand this elaboration.

4. COMPLETE CIRCUIT

The complete circuit is given in Figure 2. The following additional points should be noted:-

- (a) The "fast" and "slow" ranges are pre-selected on 5-way switches and the changeover is effected by 500 ohm P.O. type 3000 relays which are operated by supplies from the titrimeter. If the "Fast Range" relay RL1 is operated, then counting starts on the "fast" register as soon as the current is switched from the "dummy" to the cell. As the end point is approached RL1 is released and RL2 is operated; counting starts then on the "slow" register. The counting terminates when both relays release and the current is then interrupted.
- (b) Heater stabilization is provided by using the other half of the twin-triode V4 as a cathode resistance for the amplifying pentode V5. It is kept properly biased by a 3 ma drain from the -150V line. This reduces the variation due to mains voltage changes by a factor of 4.
- (c) In cases where the frequency stability of the mains supply is inadequate, provision is made for the connection of an additional timing unit. This unit is still undergoing development.
- (d) The response of the circuit to changes in mains voltage and load resistance was checked as follows. The change in voltage developed across a standard resistor in series with the load was measured for 20V. changes in the mains voltage and changes in load resistance of 500 Ω . The results are shown in Table 1.

TABLE 1

Test of Constant Current Generator.

| Range | Current | Fractional Change as Load varies from 1K to 1/2K | Fractional Change as Mains varies 20V. |
|-------|---------|--|--|
| 1 | 36.2 ma | 1/1200 | 1/7000 |
| 2 | 16.8 " | 1/1700 | 1/5500 |
| 3 | 6.87 " | 1/6000 | 1/2700 |
| 4 | 2.60 " | 1/5000 | 1/1300 |
| 5 | 1.13 " | 1/3000 | 1/900 |

- (e) The long term stability (30 minutes) of the constant current source was checked as follows. The voltage developed across a standard resistance in series with a 500 ohm load resistance was measured with a potentiometer at 30-second intervals for a period of 30 minutes. This procedure was carried out for all current ranges. In no case did the deviations from the average current exceed $\pm 0.2\%$ and was usually $\leq \pm 0.1\%$.
- (f) Since the control circuit contains only resistive elements, the response time of the circuit should be less than a few milliseconds.
- (g) The current through the cell remains constant at the set value so long as the voltage across the cell does not exceed 60V.

5. ANCILLARY EQUIPMENT

The Automatic pH titrimer, model 24 available from Electronic Instruments Ltd., Surrey, is capable of end point settings within the range pH 3-11 and mV +400 to -800. Provision is made for selected switching from "fast" to "slow" generation of the reagent within the range 0-300 mV in advance of the end point.

The indicator electrodes used in this work consisted of a Pt-W pair (10), the platinum being connected to the reference electrode terminal. Typical titrimer settings for titration of 1.7 mg of Chromium in 25 ml of water were :-

Function switch: mV Rising
End point: -50mV
Fast/slow changeover: 50mV

6. EQUIPMENT TRIALS

The complete equipment (shown in Figure 3 by means of a block diagram) was checked by the determination of varying amounts of Cr (VI) with electro-generated ferrous iron. This determination is considered typical of coulometric titrations.

Reagents

Ferric Alum Solution - Dissolve 290 g. of A.R. ferric ammonium sulphate ($\text{Fe NH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) in 200ml. of demineralised water containing 20ml. conc. sulphuric acid (S.G. = 1.84). Add 90ml. concentrated sulphuric acid and dilute to approximately 900 ml. with demineralised water. Add 30 ml. of 100 volume hydrogen peroxide, and heat to 50-70°C until evolution of oxygen is complete. Allow to cool, filter through a sintered glass disc and make up to 1 litre with demineralised water.

Potassium dichromate solution - An M/6 solution of potassium dichromate was prepared by dissolving the required amount of the dry, recrystallised A. R. salt in 1 litre of demineralised water. Less concentrated solutions were prepared from this stock solution by appropriate dilution with demineralised water.

Sulphuric Acid - 9M

Sodium sulphate solution - (5% w/v). This was prepared from the A.R. salt.

Titration cell - The titration cell used in these experiments consisted of a 100 ml. tall form lipless beaker, the electrodes being positioned in the cell by means of a bakelite jar lid which also served as a cover for the cell. The platinum cathode was of the usual "flag" type whilst the anode was a platinum wire. The sodium sulphate in the anode compartment was separated from the remainder of the solution by a sintered glass disc.

The currents were measured several times during the course of a titration by measuring the voltage produced across a standard resistor in series with the cell.

A titration is conducted in the following way. Pipette into the titration cell the required amount of ferric alum, 2 ml. of sulphuric acid and sufficient water to cover the electrodes. (Use about 5 ml. of ferric alum for sub-milligram amounts of chromium, (1-7 mA current range) and 10-20 ml. for higher generating currents.)

Set the titrimer controls as required, depress the titrimer AUTOMATIC switch and switch on the current. On completion of the pre-titration, switch off the AUTOMATIC switch and the cell. Add the solution to be analysed, record the "fast" and "slow" register readings. Depress the titrimer AUTOMATIC switch and then switch in the cell.

Measure the current at frequent intervals during the course of the titration. At the conclusion of the titration, switch out the cell and release the AUTOMATIC switch. Record the "fast" and "slow" register readings.

The best settings for the titrimeter controls are found by first carrying out a manual incremental titration. The results of automatic titrations are shown in Table 2.

TABLE 2
CHROMIUM IN POTASSIUM DICHROMATE

| Cell volume ml | mg Cr taken | mg Cr found (average) | No. of deter- minations. | Relative Mean error % |
|-------------------|----------------|--------------------------|-----------------------------|--------------------------|
| 40 | 8.67 | 8.67 \pm 0.01 | 6 | 0 |
| 25 | 1.73 | 1.73 \pm 0.01 | 4 | 0 |
| 10 | 0.173 | 0.172 \pm 0.001 | 4 | -0.6 |
| 10 | 0.0173 | 0.0178 \pm 0.001 | 4 | +2.9 |

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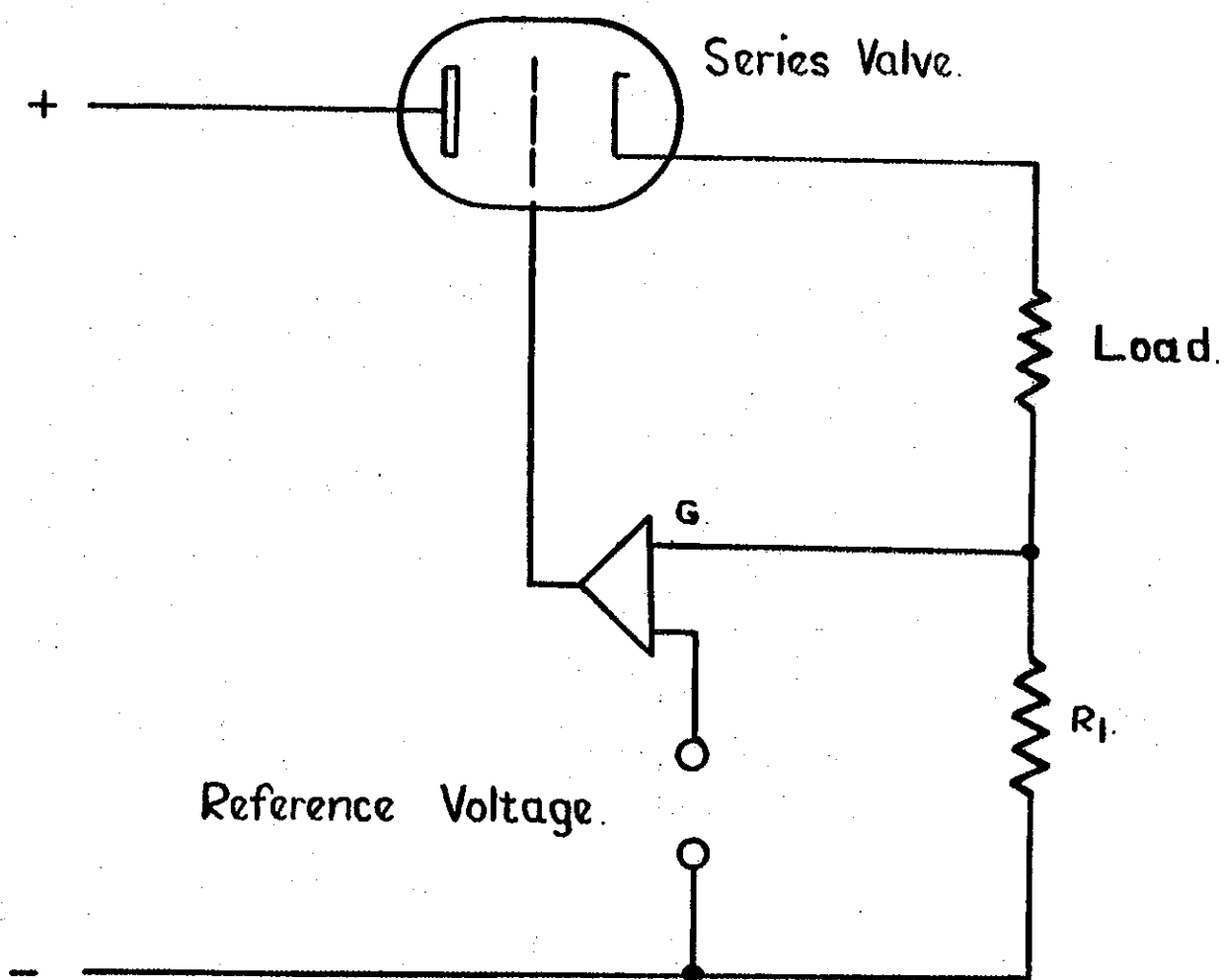
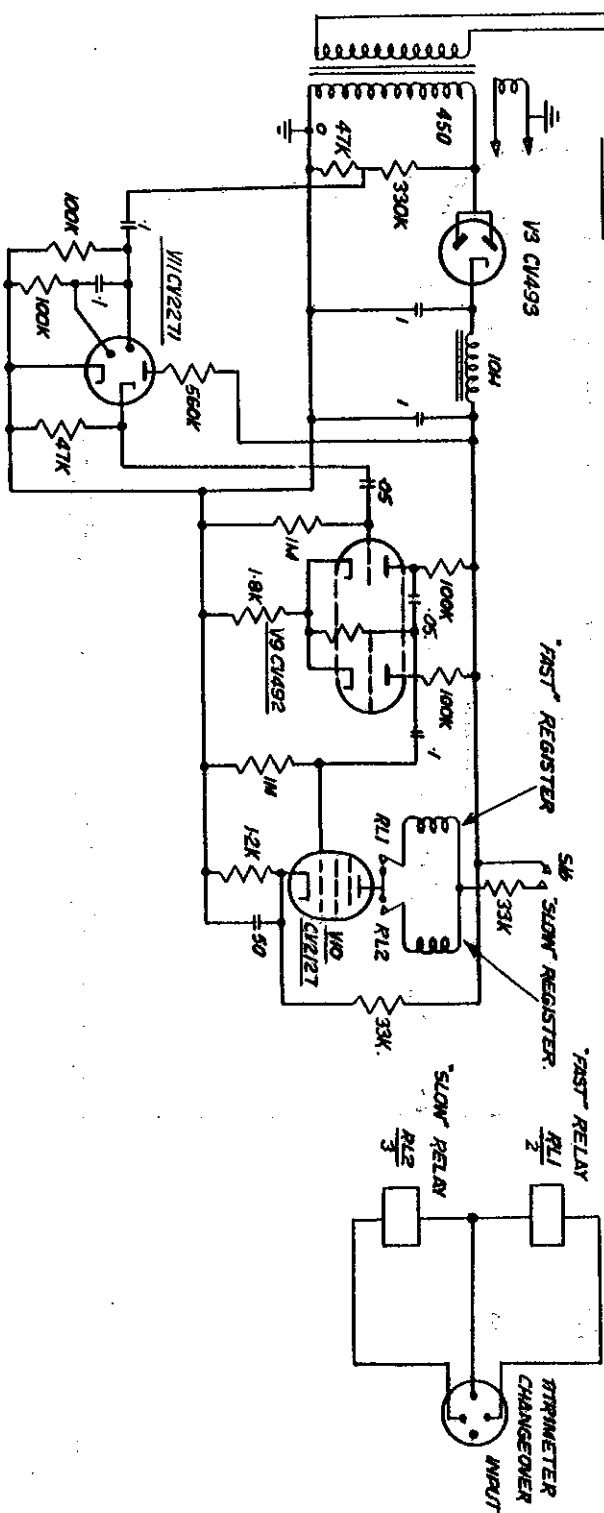
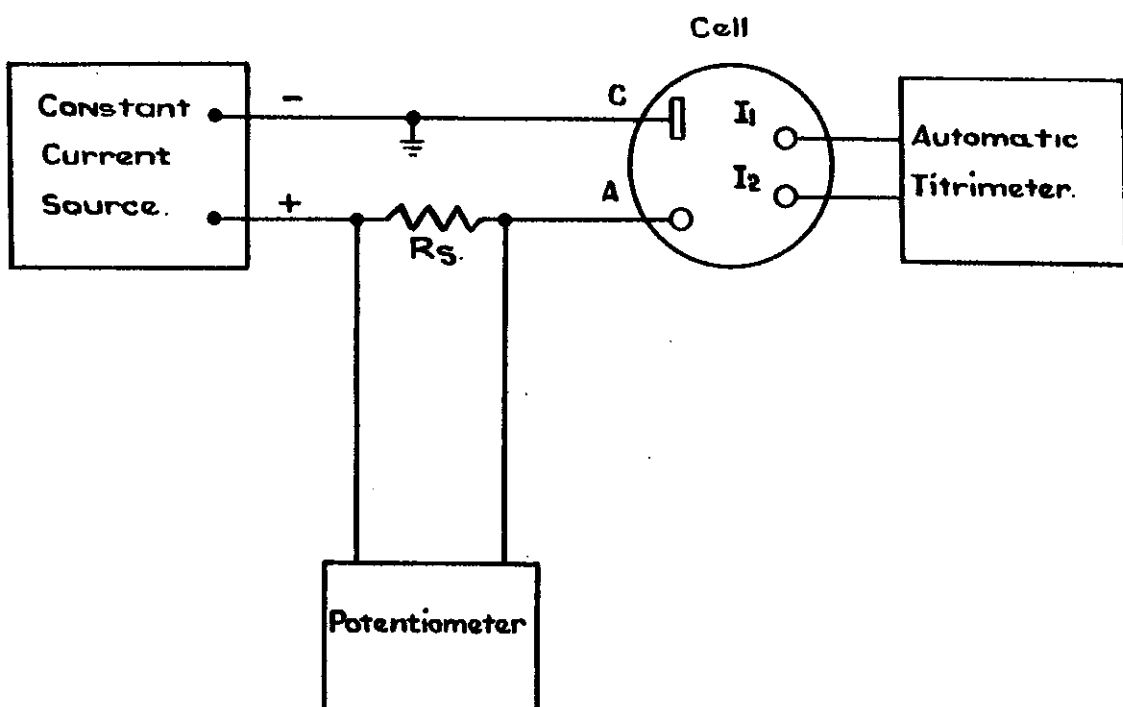


FIGURE 1.



ALL RESISTORS 1/4W GR.1



R_s = Standard Resistor.
 C = Generator Cathode.
 A = Generator Anode.
 $I_1 I_2$ = Indicating Electrodes.

FIG. 3 BLOCK DIAGRAM OF APPARTUS.

