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A New Electronic Coulometer for Electroanalytical Chemistry

Jack Donald Merry

Union College - Schenectady, NY

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*UC
Thesis*

A NEW ELECTRONIC COULOMETER
FOR ELECTROANALYTICAL CHEMISTRY

by

Jack Donald Merry

A thesis presented to the Department of Chemistry
of Union College in partial fulfillment of the requirements
for the degree of Bachelor of Science with a Major in
Chemistry.

By Jack D. Merry

Approved by

Galen W. Ewing

May 31, 1957

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Introduction

The failure of electroanalytical chemistry to apply extensively the principles of Faraday's laws, has been due primarily to the lack of a direct reading coulometer. The author has investigated several methods of current integration and has concluded that a direct current amplifier with a feedback capacitor shows best promise as a coulometer.

History

During the years 1833 and 1834, Michael Faraday published the results of an extended series of investigations on the relationship between the quantity of electricity passed through a solution and the amount of metal or other substance liberated at the electrodes. His conclusions may be expressed in the form of the two following rules:

- I. The quantities of substances set free at the electrodes are directly proportional to the quantity of electricity which passes through the solution.
- II. The same quantity of electricity sets free the same number of equivalents of substances at the electrodes.

Apparently there are no exceptions to these laws. They are independent of the concentration of the electrolyte; they are valid at all temperatures

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Gift of Author
January 8, 1958

and for all solvents. Whenever experimental results would seem to indicate an exception, one finds that an addition to the desired electrochemical change, something else has taken place. Some of the product may have been lost mechanically or converted by secondary chemical changes or there might have been leakage in the electrical system. Certainly, if all current is accounted for, Faraday's laws always hold.

The quantity of electricity required to liberate one equivalent of any substance should, according to the second law, be independent of the nature of the substance; this quantity called a Faraday, is equal to about 96,500 ampere-seconds or coulombs.

It is surprising that these principles, having been well known for more than a century, were not exploited by analytical chemists until recent years. Szebelledy and Somogyi (12) were the pioneers in this field and coined the term "coulometric analysis." They describe the method of determining the amount of a material by measuring the quantity of electricity required to affect its complete chemical change in an electrolysis cell. Lingane (6) makes the distinction between "primary coulometric analysis" and "secondary coulometric analysis". In the former, the substance being determined undergoes reaction at one of the electrodes. In the latter,

it reacts in solution with another substance generated by an electrode reaction.

The Applicability of the Method

The applicability of the method was demonstrated by the founding fathers of coulometry - Szebelledy and Somogyi - in a series of papers in the Z. Anal. Chem. in 1938. Some of the procedures which they developed are as follows:

I. Determination of Hydrochloric Acid.

Potassium chloride is added to the hydrochloric acid solution and electrolyzed, using a platinum cathode and a silver anode. A silver coulometer is used to measure the quantity of electricity. The reaction is considered complete when a bromocresol green indicator changes from yellow to yellow green at pH 3.8-5.4. The results of the analysis of 0.1 Normal hydrochloric solution in over thirty runs showed a precision of about 0.02%. Standardization of the same solution by ordinary chemical methods was precise to 0.04%.

II. Determination of Thiocyanate.

Potassium bromide is added to the solution and electrolyzed between platinum electrodes. When the reaction is complete, excess bromine imparts a yellow color to the solution, the reaction is stopped and the excess bromine is titrated. Again a silver coulometer can be used.

III. Determination of Hydrazine.

When a solution of hydrazine, potassium bromide and potassium chloride is electrolyzed, hydrogen is evolved at the cathode and nitrogen at the anode. When the reaction is complete, bromine begins to collect.

Controlled potential coulometry was originated in experiments by Hickling (3), who demonstrated that cupric ion could be determined by measuring the coulombs required for reduction to the metal on the platinum cathode. The purpose, of course, of the controlled cathode potential is to accomplish the separation of the copper from other cations which are in the solution. Hickling also developed the technique of oxidizing iodide ion to iodine coulometrically.

Lingane (4) introduced a method for successive determination of the halide ions by controlled potential coulometric analysis.

The determining factor for the accuracy of coulometric work is the current efficiency (the percentage of the total current carried by the desired electrode reaction). There must be either negligible or possibly constant secondary (undesirable) chemical reactions to get accurate results.

In all controlled potential analysis, the current approximates an exponential decay according to the following equation (as demonstrated by Lingane (8):

$$I_t = I_0 10^{-kt}$$

where: I_0 the initial current

I_t the current at time t

k is a constant

The current approaches zero (or background) asymptotically and there is thus no time when the reaction is truly complete, yet the reaction will approach sufficiently near completion that this fact is of minor analytical importance.

The Need for a Direct Reading Coulometer

The classical approach to the evaluation of the integral $\int i dt$ has always been a chemical coulometer. This is undeniably a very accurate and precise method; however, to use a silver coulometer to determine copper would merely substitute the operation of washing, drying, and weighing the silver deposited in the coulometer for the very same operations on the copper deposited in the electrolysis cell. Another example has been the use of a titration coulometer to determine the quantity of a substance which could have been titrated in the first place. A gas-liberation type coulometer, while very accurate when proper precautions are taken, is limited to micro-techniques and leaves much to be desired in the way of convenience. Turning to electronics, we find no particular problem where constant current methods are applicable but, in the case of controlled potential coulometry, the current must be free to vary. Several approaches

to the problem are reported in the literature.

The more significant attacks are the following:

1. A ball and disc integrator controlled by the pen-drive mechanism of an ordinary recording potentiometer. Its precision and accuracy was reported to be better than 1% (7).
2. Thyatron relaxation oscillator. The number of discharges through the thyatron over a period of time is proportional to the coulombs through a resistor. Accurate to within 1% as checked against a copper weight coulometer (5).
3. A low-inertia integrating motor (10). The angular velocity of the armature is a measure of the current supplied to it. Hence the number of revolutions is a measure of the quantity of electricity. A low inertia motor, with very low friction and a small time constant within its recommended range, is reproducible to around 0.1%.
4. Meites (9) reported a more accurate, but relatively complex, instrument for integration of current in controlled potential analysis. It was essentially a velocity servo system.

5. A precision coulometric integrator has been designed by Booman (1). A modified "Miller" integrator was used. This was very similar to the set-up studied by the author. It differed in the use of a high-gain D.C. amplifier with an input resistor and a "feedback" resistor. This modification results in the amplification of the original input signal. The gain is approximately the ratio of the "feed-back" resistance over the input resistance. This extends the applicability of the instrument down into the very low current range. The standard deviation was less than 0.05% over the range of 10 micro-amps through 100 milli-amps.

The first three systems, while easily applicable to techniques involving limited current variation, are not well adapted to accurate integration over as wide a range as is encountered in controlled potential analysis.

Meites velocity serve system does possess the desired characteristics and accuracy. However, because of its relative complexity and high cost, it was not given further study.

Careful consideration of all factors led the author to press in the direction of circuitry employing a high-gain D.C. amplifier with a feed-back capacitor. Although this circuit has been used as a basic component of many analog

computers, no reference of its application to electroanalytical chemistry was to be found in the literature until the work of Booman in February 1957. An interesting parallel exists between the results of Dr. Booman and of the author.

ELECTRONIC INTEGRATOR THEORY

(4) (11)

Integration in its simplest sense is a process of accumulation. Any system which will receive, store and indicate the amount of some physical quantity may be used as an integrator. Examples are chemical coulometers, watt-hour meters, wheel and disc integrators.

For the integration of a variable I with respect to another independent variable t , the following relationship is used. (fig.1)

$$Q = \int i dt$$

A capacitor will store a quantity of electricity and indicate the amount by the voltage across its plates. Thus for a pure capacitance (fig.2)

$$Q = \frac{1}{k} \int i dt$$

By using a circuit as shown in Figure 3 a current approximately proportional to ei will charge the capacitor. e must be kept small enough to avoid effecting the charging current beyond the allowable degree of approximation. A problem arises if the time interval of the integration is too great. The condenser voltage will build up to a point where it will seriously reduce the current flow, thereby introducing considerable error into the proportionality relation between ei and i . (Fig.4)

Integration is made more accurate and practical by the use of a high-gain negative feed-back computing amplifier. The circuit is shown in figure 5.

$$e_o = - e_1 \frac{t}{RC}$$

Whence

$$e_o = \frac{1}{RC} \int e_1 dt$$

We see this is the same relationship as for an ordinary capacitor circuit except the time constant of the integrating unit is effectively increased by a factor of A times. This means that we may integrate for a period of A times as long with similar error, or for the same period with the error decreased by a factor of approximately $1/A$.

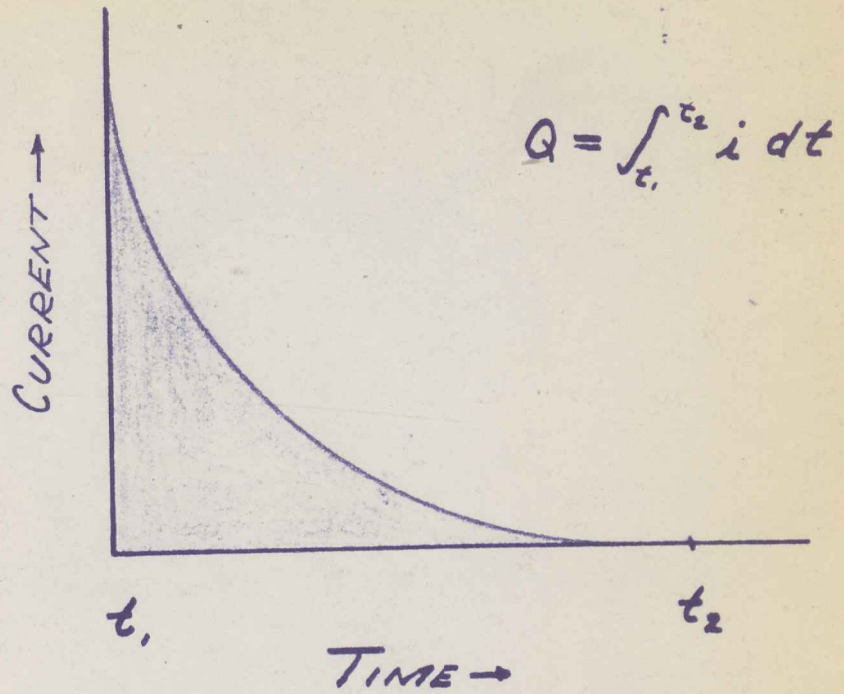
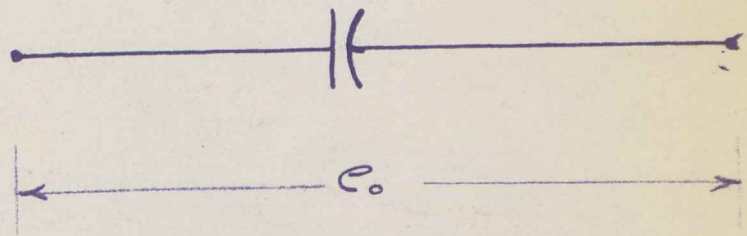


fig. 1



$$e_0 = \frac{1}{c} \int i dt$$

fig. 2

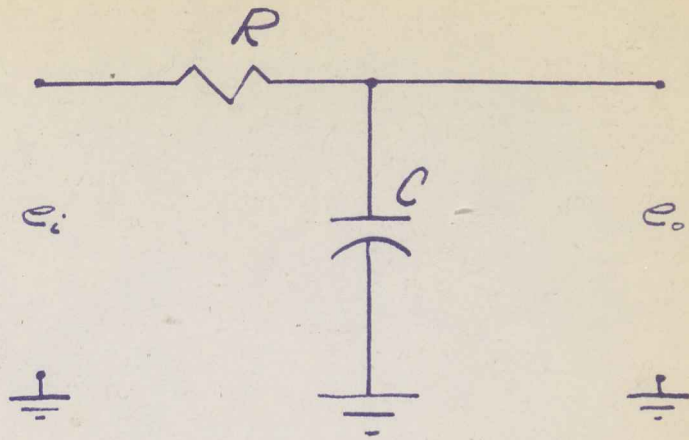


fig. 3

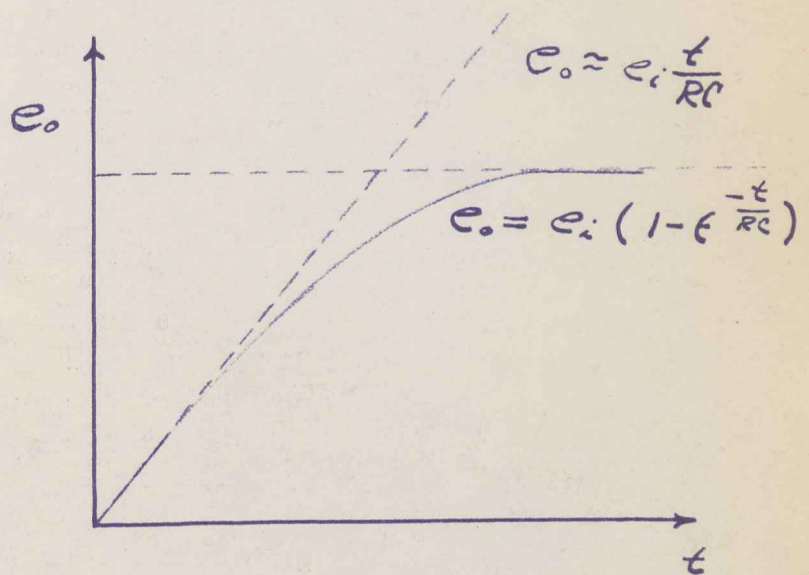


fig. 4

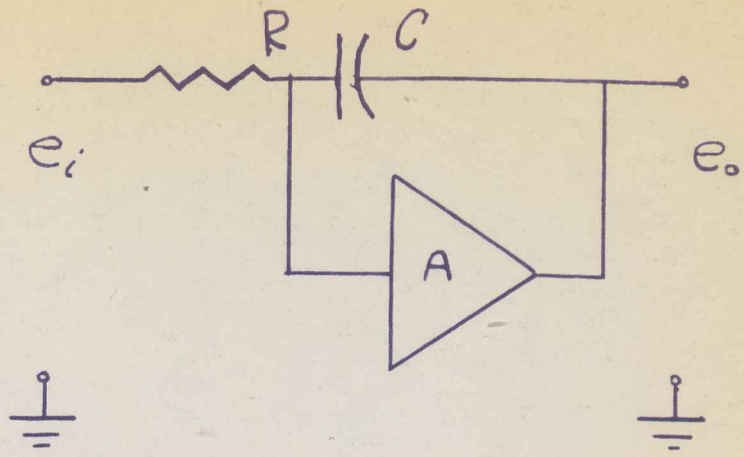


fig. 5

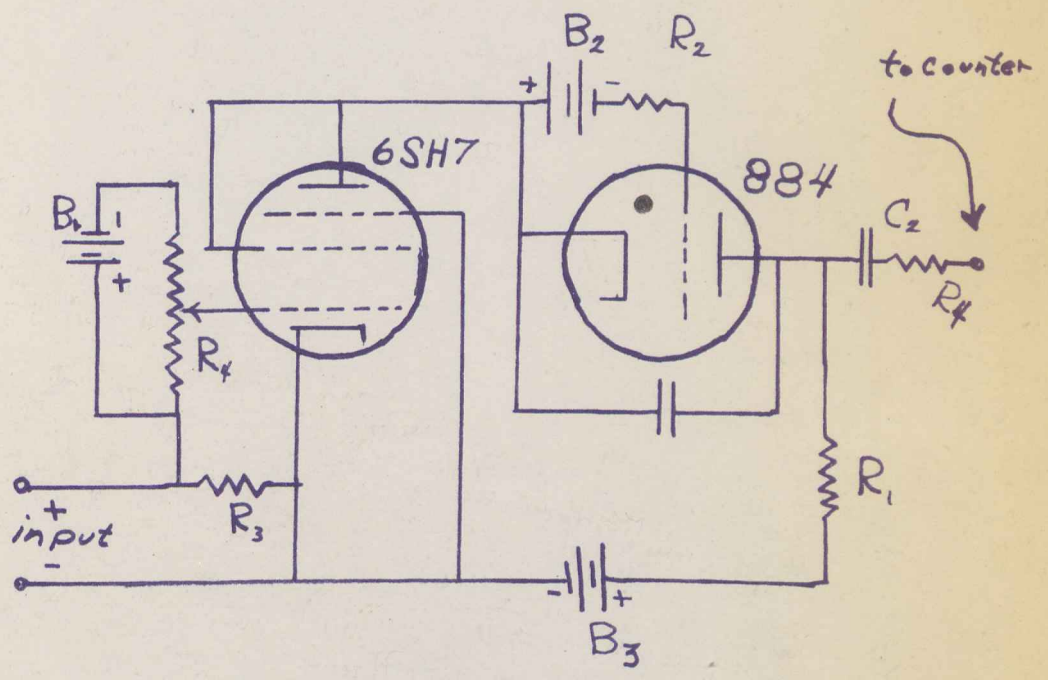
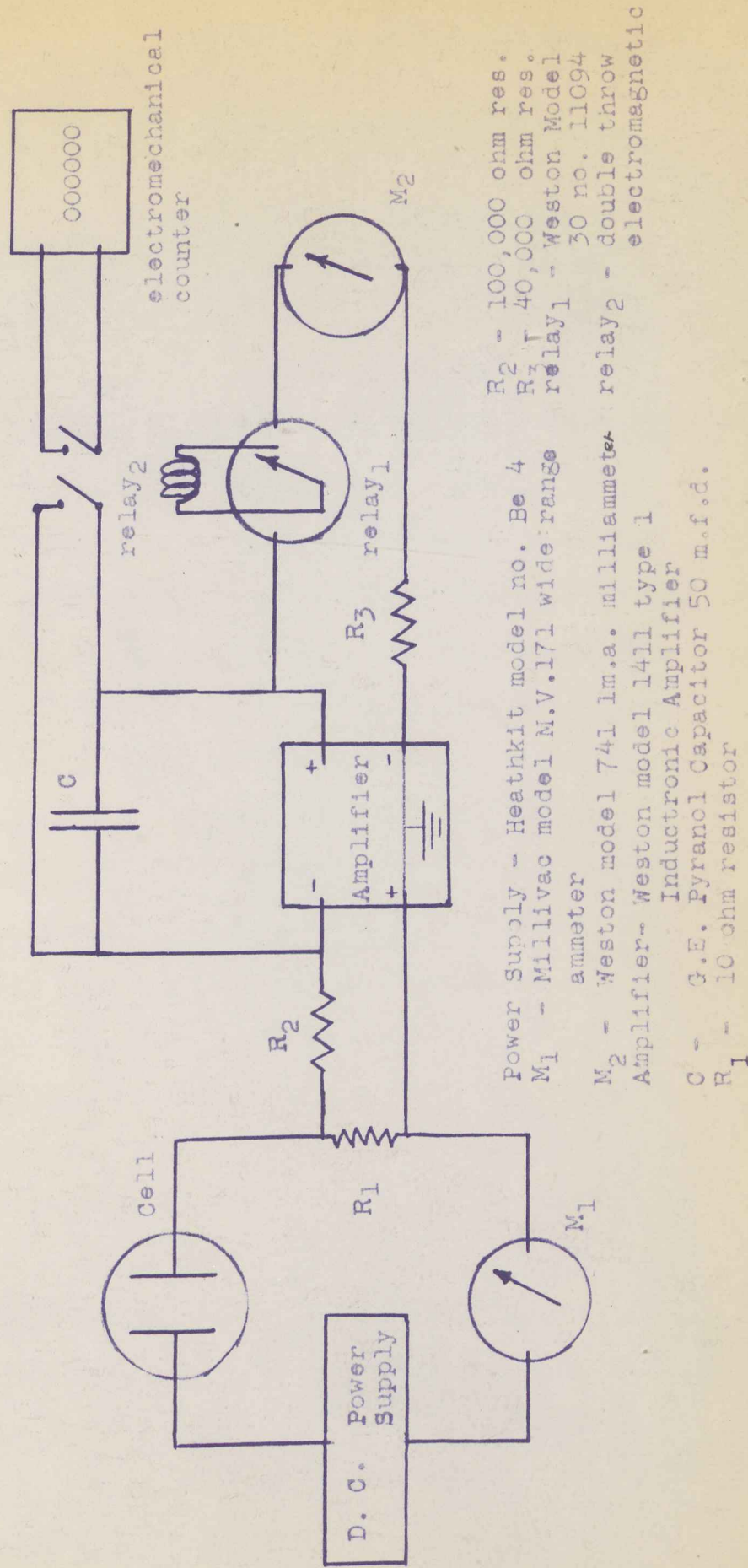


fig. 6



- Power Supply - Heathkit model no. Be 4
- M₁ - Millivac model M.V.171 wide-range ammeter
- M₂ - Weston model 741 1m.a. milliammeter-relay
- Amplifier - Weston model 1411 type 1 Inductronic Amplifier
- C - G.E. Pyranol Capacitor 50 m.f.d.
- R₁ - 10 ohm resistor
- R₂ - 100,000 ohm res.
- R₃ - 40,000 ohm res.
- relay - Weston Model 30 no. 11094 double throw electromagnetic

fig. 7

Experimental Results

I. An electronic coulometer patterned after Kramer's (5) circuit (Fig.6) was constructed. The circuit is basically a thyatron relaxation oscillator, modified by a frequency control. The total number of discharges through the thyatron is a measure of the quantity of electricity passed through the reference resistor. The counts per coulomb should be constant over the input range. This constant is a function of the linearity of the amplifier, the reproducibility is dependent upon the quality of the thyatron.

The instrument was studied by supplying a constant input voltage and recording the number of counts per ^{unit} limit of time. Hence the quantity of electricity passed through the resistor was directly proportional to the voltage input. The relationship of the counts per minute to the input voltage should be a straight line. The actual results strayed as much as 5 per cent (though in a reproducible manner). At times the instrument would refuse to function at counting rates below about 40 counts /minute. The resulting operating input range was only from about 1 volt to 15 volts. This would be a range of 0.100 amps to 1.5 amps for a 10 ohm reference resistance. Because the apparatus did not function over the desired range nor with desired accuracy the author abandoned the

thyatron relaxation oscillator at turned his attention to the construction of a D.C. amplifier and feed-back capacitor arrangement.

II. It was found that the build up rate of the integrator was inversely related to the capacitance of the feed-back capacitor, the resistance of the out-put circuit, and the value of input resistor. The relation of the capacitor is explained in the theoretical treatment. The input resistor by a simple Ohms-law relationship for parallel circuits lowers the current to the amplifier for a given cell current. This results in a lower current through another resistor within the amplifier which therefore results in a lower e_i signal to the integrating mechanisms. The explanation of the function of the output resistor is that the amplifier is connected as a current amplifier thus an increase of resistance in the output circuit requires an increase of the output potential to maintain the current amplification. Hence the voltage amplification is a function of the output resistor.

For lower values of capacitance, input resistance or output resistance radio wave pickup and capacitor charge decay were major problems. The application of the integrator to analytical chemistry requires measurements of relatively large quantities of electricity. To increase the number of coulombs represented by full scale deflection of the output meter either the capacitance or the input resistance must be increased. The sensitivity of the integrator

decreases with increasing input resistance and unaccounted for effects cause a build-up of the output which is not an accurate measure of the input coulombs. A capacitor of the necessary range for our application would result in a package of unmanageable size and considerable expense. For accurate integration the capacitor must have very low leakage and very low dielectric absorption. A 50 mfd oil filled capacitor was decided upon as a compromise between size, reliability of integration and cost.

For even the slowest practical build-up rate the number of coulombs represented by full scale deflection was still too low for application to electroanalytical chemistry. This problem was resolved by the introduction of a D' Arsonval relay to the output circuit in series with the Millam-meter. The relay was connected to trigger a second relay when a current of more than 1 ma flowed through its coil. This second relay in turn triggers an electro-mechanical counter and simultaneously discharges the feed-back capacitor. With the capacitor discharged the integrator begins another cycle. The total number of coulombs is determined from the number of cycles recorded on the counter and the residual reading on the milliammeter.

Calibration

I. The integrator was checked against a copper weight coulometer with the following results for 15 cycles.

Current (amperes)	Wt of Copper (Grams)	Coulombs from copper coulometer	Coulombs/ count
1.0	0.1066	323.3	21.55
1.0	0.1064	323.0	21.53
1.0	0.1067	323.9	21.59
0.5	0.1064	323.0	21.53
0.030 to 1.40	0.1061	321.1	21.47
0.030 to 1.40	0.1061	321.1	21.47
0.030 to 1.40	0.1059	321.2	21.41
AVERAGE			21.51
STANDARD DEVIATION			0.06

II. A constant current of 20 milliamperes was supplied to the integrator for one cycle with a resulting time interval of 425 seconds or 21.3 coulombs/count.

Discussion

The results in the table indicates excellent agreement over the whole range studied. It is quite probable that the apparatus would function well at both higher and lower currents than were studied.

Possible improvements would include:

- (1) A resistor with better heat dissipation for higher current applicability.
- (2) A more dependable electromechanical counter.
- (3) The calibration of the coulombs/count as a function of R_2 leading to the use of a variable resistor as a range switch.

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