

Precise Wide-Range Direct-Reading Electronic Integrator

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A PRECISE wide-range direct-reading integrator may be assembled from a d.c. potential to an a.c. frequency converter and an electronic counter. This integrator is useful in controlled-potential coulometry and in gas chromatography.

In the block diagram shown in Figure 1, the d.c. signal to be integrated may be the voltage drop across a resistor in series with a current to be integrated. This voltage is fed to the converter, where an a.c. signal is generated the frequency of which is directly linearly proportional to the magnitude of the d.c. signal. At a typical range-setting of the converter, its output will vary from 0 to 10,000 cycles per second when its input varies from 0 to 1.000 volt d.c. The cycles of the a.c. frequency output of the converter are then counted by the electronic counter. The total number of a.c. cycles counted is directly linearly proportional to the quantity of electricity which has passed through the series resistor in the original circuit.

A selection of the values of the series resistor and of the converter range may be made to provide direct-reading of the counter in coulomb units. For example, when a series resistor of 100.00 ohms is used with a converter range of 0 to 10,000 cycles per second for a 0 to 1.000-volt input, a current of up to 10 ma. may be integrated with the counter reading directly in microcoulombs.

Because in controlled-potential coulometric titrations a current of 96.5 ma. will produce one micro-equivalent of electrochemical change per second, the use of a 10.363-ohm series resistor in the electrolysis circuit with the same converter range as above will result in each count of the electronic counter representing 100 picoequivalents of electrochemical reaction.

We have used a Hewlett-Packard Dymec Model DY-2210 converter and a Nuclear-Chicago Model 192-B scaler to integrate over periods of from a few seconds to 30 minutes with a precision of from $\pm 0.02\%$ to $\pm 0.05\%$. Other brands of converters are available with

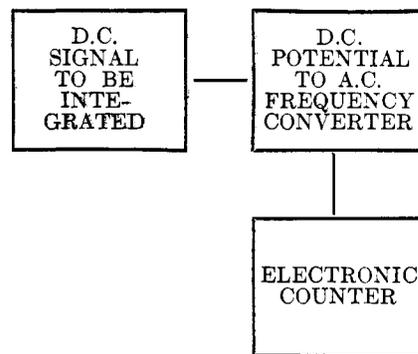


Figure 1. Block diagram of integrator

more or less precision, depending on price, and any electronic or electronic-mechanical counter having a counting speed of at least 10,000 counts per second may be used.

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High Speed Coulometer Based on a Voltage-to-Frequency Converter

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A COULOMETER used in controlled potential coulometry should be accurate, linear, capable of following rapid changes in current, and easily constructed. Ideally it should indicate directly coulombs or equivalents and should require only a small voltage input. The coulometers most frequently used (4) generally fail in one or more of these requirements. Although chemical coulometers, such as gravimetric, titra-

tion, and gas coulometers, are inexpensive and easily used, they are not useful for the coulometric determination of very small amounts of material and they require many manipulations and calculations before results are available. Electromechanical coulometers, such as those based on the ball and disk integrator, are incapable of following very rapid changes in current, while direct current integrating motor types are non-linear and require input voltages of as much as 24 volts. Integrators based upon a high quality capacitor and an operational amplifier (2) meet most requirements.

Kramer and Fischer (3) have described a coulometer based on a simple relaxation oscillator-counter combination. The accuracy of this instrument was only within 1% and its linearity was not checked over a very wide current range. We have constructed a highly accurate and sensitive coulometer based on an integrating amplifier-type voltage-to-frequency converter which may be assembled readily from commercially available components. The coulometer presents the number of coulombs in digital form on a counter

and may be used in rapid electrochemical determinations where electrolyses are completed in about 60 seconds.

EXPERIMENTAL

The assembly of the coulometer is shown in Figure 1. Its operation is based on the ability of a converter to produce output pulses of a frequency proportional to the voltage applied to its input. When this output frequency is applied to a counter, the accumulated number of counts is proportional to the voltage-time integral. For use as a

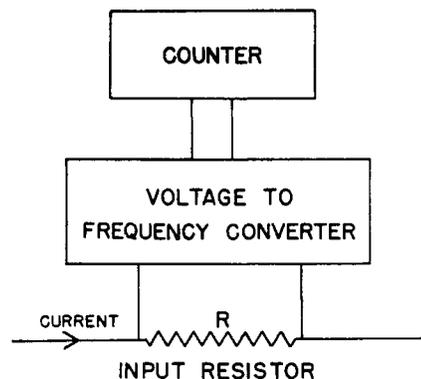


Figure 1. Block diagram of coulometer

Table I. Effect of Variation of Input Current at Constant Input Resistance on Calibration Factor of Coulometer

(Input resistor was 10.000 ± 0.005 ohm)

Current, Ma.	Calibration Factor, Counts/Volt-sec.
70.872	10,015
67.306	10,011
6.6794	10,009
0.7139	10,000
0.08501	10,104

Table II. Effect of Variation of Input Resistance on Calibration Factor of Coulometer

Current, μ a.	Resistance, Ohms	Calibration Factor, Counts/Volt-sec.
High Resistance		
85.01	10	10,104
84.94	100	9,993
84.98	1,000	9,987
51.88	5,000	9,955
152.91	5,000	9,955
84.77	10,000	9,902

Current, Ma.	Resistance, Ohms	Counting Rate, Counts/Sec.	Calibration Factor, Counts/Volt-sec.	
			Found	Corrected ^a
Low Resistance				
6.6487	100	6650.0	10,002	10,000
6.6484	10	665.67	10,013	9,993
6.6481	1	67.37	10,134	9,935
6.6481	0.1	7.791	11,723	9,731

^a Corrected for terminal resistance of plug-in resistor (0.017 ohm).

coulometer, the voltage drop produced by the electrolysis current passing through a standard resistor is applied to the converter input.

The apparatus comprised a Dymec Model DY-2210 (Hewlett-Packard Co., Palo Alto, Calif.) voltage-to-frequency converter, which produces a full-scale frequency output of 10,000 cycles per second for a 1-volt input and zero cycles per second with a zero input. The accuracy of the conversion is within $\pm 0.06\%$ of full scale, and the linearity is specified as within $\pm 0.005\%$ of full scale. The converter zero drift was less than 6 counts per hour. The counter used was a Radiation Instrument Development Laboratory Model 210 scaler with a 0.8- μ sec. resolving time. Most commercially available counters are capable of counting 10,000 pulses per second, and can also be used.

Table III. Use of Coulometer in Controlled Potential Coulometric Determination of Silver

(Supporting electrolyte, 1M KNO₃; input resistor, 1,000 ohm)

Coulometer Reading, Counts	Silver, μ eq.	
	Back-ground	Taken
Total	Found	Found
A. Long electrolysis times (20 min.); volume, 150 ml.		
237,365	570	246.5
237,593	180	246.5
238,796	1,800	246.5
Av. found = 245.7 μ eq.; average error = -0.3%		
B. Short electrolysis times (100-160 sec.); volume, 7 ml.		
24,569	312	25.01
23,945	205	25.01
24,013	190	25.01
24,594	200	25.01
Av. found = 24.94 μ eq.; average error = -0.3%		

In the calibration and testing of the coulometer, a Model S-1 timer (Standard Electric Time Co., Springfield, Mass.), with an accuracy of ± 0.002 second, was employed. The input current to the converter, maintained constant to within $\pm 0.01\%$, was determined by measuring the voltage drop over a General Radio Type 500 resistor, accurate to $\pm 0.05\%$, with a Leeds & Northrup Model 8687 potentiometer.

RESULTS AND DISCUSSION

To test the linearity of the coulometer at a constant input resistance, the voltage drop over a 10,000-ohm resistor, with currents of 85 μ a. to 71 ma. passed for known time intervals, was measured. Table I indicates that the linearity over this approximately thousandfold range of current change is better than 0.1% except at the very lowest range, where it is still within 1% of the calibration at higher currents. Each result in Table I represents the average of at least two measurements, whose reproducibility was always within 0.06%. This highly linear behavior of the coulometer allows direct application to controlled potential coulometric determinations, where the current is usually allowed to decay to about 0.1% of its initial value, without correction.

The effect of variation of the input resistor on the calibration of the coulometer is shown in Table II. As the input resistance increases, the calibration factor, in counts per volt-second (or counts per coulomb-ohm), decreases. This decrease begins to become significant with input resistors of greater than 1000 ohms. The input resistance of the voltage-to-frequency converter is about 1 megohm, so that the input resistor is effectively in parallel with a 1-megohm resistor. At high values of input resistors this 1-megohm shunt becomes sig-

nificant, so that with a 1-megohm input resistor, the calibration factor would decrease to about 5000 counts per volt-second. In practical coulometric determinations this is of little consequence, since the coulometer can be calibrated with the input resistor held constant. At very low input resistor values, the terminal resistance of this resistor, about 0.02 ohm with plug-in resistors, becomes important, so that it is generally inadvisable to use input resistors smaller than 1 ohm. For integration at current levels above 1 ampere, the front panel voltage attenuator of the converter can be employed to change the full-scale voltage input of the converter to 10, 100, or 1000 volts. Because the linearity of the converter is ± 0.5 count per second ($\pm 0.005\%$ of full scale), appreciable errors may occur at very low counting rates. The error is the calibration factor with a 0.1-ohm input resistor (Table II) illustrates this behavior. Although this error will generally be insignificant in coulometric determinations because most counts are accumulated at high counting rates, for highest accuracy, it is desirable to have the input resistor of such a value that the voltage drop caused by the initial current is about 1 volt.

The coulometer was tested under actual controlled potential coulometry conditions by carrying out electrolyses in various cells at several electrolysis rates (Table III). The digital output of this coulometer made background current corrections very simple to apply. The coulometer was allowed to count for a preset time interval appropriate to the electrolysis conditions. The total counts for the electrolysis were recorded, the background level was counted for a specified time, and the background counts were subtracted from the total counts accumulated during electrolysis. Because the potentiostat employed here had a maximum output voltage of only 24 volts, coulometers, such as those based on a direct current integrating motor, which require a large input voltage for operation, could not be employed. Under conditions of high speed controlled potential coulometry (1), the total electrolysis times are about 100 seconds, so that electromechanical coulometers, such as ball and disk integrators, which cannot follow very rapid changes in current, cannot be used.

With this coulometer, the total amount of electricity in coulombs, Q , is given by:

$$Q = \frac{N}{10,000 R} \quad (1)$$

where N is the total number of counts and R is the value of the input resistor in ohms. The smallest amount of electricity that can be practically measured with the coulometer can be estimated

by assuming use of a 1-megohm input resistor, which produces a counting rate of only about 5000 counts per coulomb-ohm. Under these conditions the coulometer will record 2×10^{-7} coulomb, or 2×10^{-6} microequivalent, per thousand counts. This number probably represents the lower limit of usefulness of this coulometer. Some potentiostats, such as the type used in these determinations, operate with the working electrode at ground potential. The voltage-to-frequency converter cannot be used directly with these potentiostats, because one of the input terminals is grounded through the line cord and the chassis. With these conditions, the converter must be insulated from the chassis of the potentiostat and connected to the line via an isolation transformer. The counter may also have to be floated

in a similar manner. This was employed during the above determinations, and the coulometer continued to operate in a satisfactory manner.

The major drawback to this system is its relatively high cost (\$650 for the converter). This is compensated somewhat by negligible construction costs: The converter can be used immediately as a coulometer, simply by connecting it to a counter. The ease of operation of the coulometer makes its application to controlled current coulometry (coulometric titrations) attractive. It is free from the usual start-stop errors of mechanical clocks and does not require a constant current for titration. By using a counter with an accurate gate time, the converter-counter combination may also be employed as a digital voltmeter. The coulometer should

prove suitable for automatic analysis, because the output of the counter can operate a digital recorder, and by proper choice of input resistor, it may be made to read directly in microequivalents, grams, etc.

LITERATURE CITED

- (1) Bard, A. J., submitted for presentation, Division of Analytical Chemistry, 142nd Meeting, ACS, Atlantic City, N. J., September 1962.
- (2) Booman, G. L., *ANAL. CHEM.* **29**, 213 (1957).
- (3) Kramer, K. W., Fischer, R. B., *Ibid.*, **26**, 415 (1954).
- (4) Lingane, J. J., "Electroanalytical Chemistry," 2nd ed., pp. 339-50, 452-60, Interscience, New York, 1958.

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A Simple Qualitative Ashing Microtest for Organosilicon and Other Organometallic Compounds

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IN THE COURSE of studies on synthetic organosilicon compounds, questions frequently arose as to whether a given substance isolated from a reaction mixture contained the desired metallic or metalloidal atom. Ultraviolet absorption spectra proved useless, while infrared spectra were not always unequivocally interpretable, particularly for complex molecules containing certain functional groups. Quantitative microanalysis was not economical or rapid enough for our purpose either.

Most of the qualitative tests for silicon in organic compounds are based on chemical cleavage processes which yield silica. These include hydrolyses and/or wet oxidations with fuming nitric acid (4), sulfuric acid alone (8) or in conjunction with potassium permanganate (13) or with glacial or nitric acid (7), 60% perchloric acid (a good quantitative procedure also) (5), hydrochloric acid or sodium hydroxide with subsequent acidification (for silicon orthoesters and siloxanes) (9, 11), and fusion with sodium peroxide mixtures in a Parr bomb (12, 16) or a platinum wire loop (10).

Although the concept of burning the unknown substance and examining the residue for silica is well established (14), the literature is vague on a reliable procedure. Eaborn (2) claims that the method of burning a drop of material on a glass rod beneath a cold glass sur-

face works "reasonably well even with volatile substances." However, we find that carbonaceous smoke from aromatic silanes obscures this test. Other references (1, 15) cite combustion as a suitable test but give no details or critical evaluation of its scope and reliability.

In our hands, the conventional methods for burning a sample to produce silica—such as holding the material in a flame or furnace with a spatula, wire loop, rod, crucible, or other container—were not only wasteful of material but also did not yield consistently reliable results. Combustion of a sample at the open end of a glass capillary tube succeeded in giving a visible ash for some highly and moderately volatile alkylsilanes but failed with aromatic silanes. These latter usually produced a carbonaceous deposit which was difficult to oxidize and readily fused

into the glass with no sign of the expected silica ash.

A simple assembly and a reliable experimental procedure have been developed which gave, with proper combustion technique, a white silica ash from each of more than 40 different organosilicon compounds of varying volatility, structure, composition, and thermal stability. For solids, a 1-mg. sample generally proved more than sufficient, although liquids, particularly the more volatile ones, usually required more material. With greater refinement such as the use of a smaller assembly, a microburner, and examination under a microscope, this method may be successfully used with even less sample.

EXPERIMENTAL

Apparatus. The assembly (Figure 1) consists of a 5-cm. length of nichrome or platinum wire, about 0.8 mm. in diameter, with a hook of 0.8 mm. radius at one end. The wire is then passed through a borosilicate glass melting point capillary, about 1.6 mm. o.d. and 1.5 to 2 cm. long, until the hook contacts the glass, and then about 1 cm. into a length of thick-walled glass capillary tubing (1 mm. bore) which serves as a handle. The wire is bent slightly near each end to keep it from slipping out of the handle and also to keep the thin-walled capillary from sliding.

Procedure. About 1 mg. of powdered sample or a small drop of liquid is collected in the hook; if a solid, the sample is melted onto the hook by warming it near a flame. For the ashing procedure, a Bunsen burner

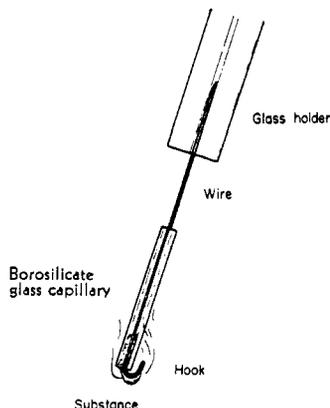


Figure 1. Assembly

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