ELECTROGENERATION OF BROMINE BY A PULSE TECHNIQUE FOR COULOMETRIC TITRATIONS

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INTRODUCTION

A coulometric technique using pulses of constant magnitude has been described by DEVANATHAN AND FERNANDO[1]. In the instrument that they described, pulses of constant magnitude were generated with the aid of a multivibrator and electromechanically counted. A constant pulse size was achieved by using a high stability power supply of relatively complex design. It was considered useful to investigate the performance of this instrument when the power supply was replaced with a simplified or a readily obtainable power pack. Two such power supplies have been used in this work, a conventional power pack regulated with "Barretter tubes", and a Healthkit Model PS-3 power supply. The constancy of the current pulses generated by this simplified multivibrator has been tested directly by means of a silver as well as a copper coulometer, and indirectly by titrating arsenic(III) and 8-quinolinol with electrogenerated bromine.

The indicator circuit has also been studied in order to determine the optimum conditions for the amperometric detection of the end-point in bromometric titrations.

EXPERIMENTAL

Coulometric titrations with electrogenerated bromine

Fig. 1 shows the multivibrator circuit used. A Healthkit Model PS-3 "Variable Voltage Regulated Power Supply" served as the source of anode voltage. Steady anode voltages were obtained about 15 min after switching this device on. Switches S_1 and S_2 permitted the selection of one of three resistances, 100 KΩ, 500 KΩ and 1 MΩ as the grid bias of the tubes V_1 and V_2. Consequently nine combinations of R_1 and R_2 were possible, seven of which were found to allow the generation of pulses at a steady rate when $B+$ was 250 V. If $B+ = 200$ V it was found that all combinations of R_1 and R_2 gave pulses at a steady rate (Table I). The magnitude as well as the rate of generation of the current pulses are critically dependent on the anode voltage and the values of C_1, C_2, R_1 and R_2. Switch S_3 was used to short circuit the cathode of V_2 to ground so as to permit the multivibrator to run freely when not connected to the titration cell. A high speed relay, which operated an electric counter, was

connected on the anode line of V_2 and the titration cell was connected between the cathode of V_2 and earth.

The titration cell consisted of a central flat-bottomed vessel in which the generator cathode and a platinum indicator electrode were placed. Two side arms were fused on either side of the central vessel; these were saturated calomel reference electrodes
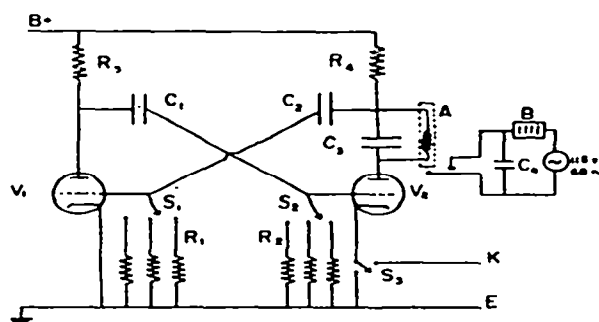

Fig. 1. Multivibrator circuit.

C_1	1 μF (mica);	B	Pic Electric Counter Model 6115A;
C_2	0.5 μF (mica);	K and E	connections to titration cell;
C_3	2 μF;	R_1	100 KΩ, 0.5 MΩ and 1.0 MΩ;
C_4	0.1 μF;	R_2	100 KΩ, 0.5 MΩ and 1.0 MΩ;
V_1 and V_2	6 SN7;	R_3	15 KΩ Ohmite 50 W;
A	Potter and Brumfield Plate Circuit	R_4	10 KΩ Ohmite 50 W.
	Relay KCP 5/5 KΩ;		

TABLE I

VARIATION OF PULSE HEIGHT WITH R_1 AND R_2

$B+ = 250$ V; load $= 47$ Ω.

$R_1 : R_2$ (KΩ : KΩ)	Maximum height (scale divisions)	Maximum height (scale divisions)
100 : 100[a]	+ 9.1	—2.7
500 : 100	+ 8.0	—5.0
1000 : 100	+ 8.4	—4.4
100 : 500[a]	+11.2	—3.0
500 : 500	+ 7.5	—5.0
1000 : 500	+ 7.9	—4.5
100 : 1000	+11.4	—3.0
500 : 1000	+ 7.2	—5.0
1000 : 1000	+ 7.9	—4.2

[a] The rate of generation of pulses is not constant.

and were separated from the central compartment by sintered discs and agar plugs. One of the reference electrodes and the platinum generator cathode were connected to E and K respectively in the multivibrator circuit shown in Fig. 1. The second reference electrode and a platinum electrode of area 5.38 cm^2 were used as the indicator electrodes. A platinum microelectrode, rotated at a speed of about 600 rev/min with a Sargent synchronous motor was also used as an indicator electrode and proved to be far superior to the platinum foil electrode. The saturated calomel reference electrode and the platinum indicator electrode were connected to an R.C.A. ultrasensitive d.c. microammeter. The potential of the saturated calomel electrode was sufficiently

negative to give limiting currents which were proportional to the concentration of free bromine in solution. It was found convenient in some experiments to record the limiting current, and a Speedomax Type G recorder was used for this purpose. In all experiments the solution in the central titration vessel was stirred vigorously by means of a magnetic stirrer.

Electrodeposition of copper and silver

The pulse circuit and counting circuit were the same as that described by DEVANATHAN AND FERNANDO[1]. The power supply consisted of a conventional power pack with a full wave rectifier, choke and condensers regulated at 300 V with the aid of two VR 150 tubes. The current was supplied to all apparatus through a constant voltage transformer delivering 230 V a.c. at 50 cycles.

The cell in which electrodepositions were carried out consisted of a platinum crucible containing the electrolyte. The crucible was placed on a conducting surface and connected to the cathode. The anode consisted of a cylindrical block of silver 25 mm long and 12 mm in diameter to which was screwed a long silver rod 3 mm in diameter. This rod was clamped with the aid of a polythene sleeve insulator, so that the cylindrical anode was symmetrically placed in the electrolyte. A similar copper anode was used for the electrodeposition of copper.

In order to carry out electrodepositions at elevated temperatures, the platinum crucible was inserted into a cavity machined out of a brass hexagonal block, 10 cm high. This block was heated electrically on a hot-plate, the block being insulated from the hot-plate by a mica sheet. A thermometer pocket, in close proximity to the cavity in the brass block, registered the temperature of the bath solution.

Two different electrolytes were used in the electrodeposition of silver. The first electrolyte consisted of 250 ml of 0.1 M $AgNO_3$ to which concentrated ammonia was added until a faint permanent precipitate was obtained. To this solution, 30 g CH_3COONH_4 and 10 g NH_4NO_3 were added, and the resulting solution stirred thoroughly and filtered before use. The second electrolyte was prepared by mixing 250 ml of 0.1 M $AgNO_3$ and 250 ml of 0.5 M KCN. The solution was filtered before use. The electrodeposition of copper was carried out from the following solution: concentrated ammonia was added to 250 ml of 0.5 M $CuSO_4$, until a faint permanent precipitate was obtained. To this solution, 30 g CH_3COONH_4 and 10 g NH_4NO_3 were added and the resulting solution thoroughly stirred and filtered before use.

TABLE II

ELECTRODEPOSITION OF COPPER AND SILVER WITH CURRENT PULSES

Metal	Time (min)	No. of pulses	Wt. of metal (mg)	No. of determinations
Silver	30	2145 ± 8	17.91 ± 0.22	11
Silver	30	2146 ± 7	18.19 ± 0.21	14
Copper	60	4294 ± 11	10.24 ± 0.11	15
Copper	60	4290 ± 13	10.61 ± 0.03	6
With new tubes in multivibrator				
Silver	30	2327 ± 8	16.23 ± 0.15	15
Copper	60	4667 ± 8	8.75 ± 0.16	12

The pulse coulometer was switched on and allowed to warm up for about an hour with the cell connections short circuited. The high voltage supply to the multivibrator circuit was switched off leaving the filament current on. The connections to the coulometer were made and the high voltage supply switched on. Current pulses were passed for a fixed period of time, the high tension supply switched off, and the number of pulses passed was noted. The platinum crucible was washed repeatedly with distilled water until it was free of electrolyte, rinsed with methanol, dried at $130°$ in an oven, cooled in a desiccator and weighed on a microbalance to the nearest hundredth of a milligram. The results obtained are shown in Table II.

RESULTS

The shape and size of current pulses

The shape and size of current pulses obtained from the simple multivibrator circuit shown in Fig. 1 were studied on a cathode ray oscilloscope. The voltage across a resistance of $47\ \Omega$ connected between the points K and E, was applied to the Y plates of an oscilloscope with $R_1 : R_2 = 100\ K\Omega : 100\ K\Omega$. Pulses were generated at a suffi-
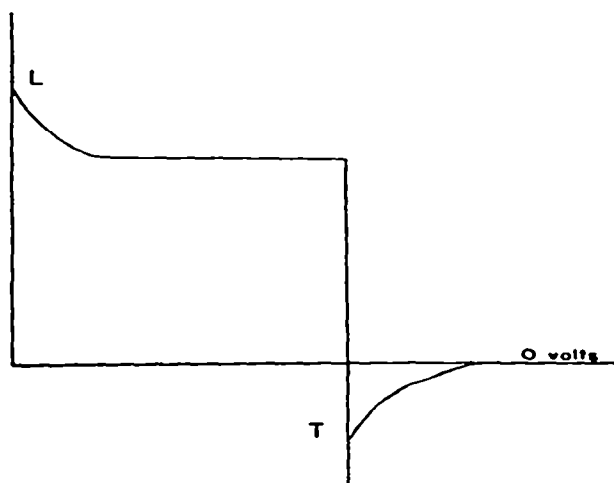

Fig. 2. Pulse shape obtained with multivibrator.

ciently rapid rate to permit the sweep frequency to be adjusted to give a stationary image on the screen, the general shape of which is shown in Fig. 2. Each pulse had a leading edge L over the flat portion of the pulse and a trailing edge T below the zero voltage line. The pulses were found to be of constant magnitude. The shape of the pulse was not altered significantly by disconnecting the relay and connecting the anode of V_2 to $B+$ through a bias of $10\ K\Omega$. The maximum heights of the leading edge at a $B+$ of 250 V for each combination of R_1 and R_2 are given in Table I. An asterisk denotes those combinations which do not permit a steady generation of pulses at $B+ = 250$ V.

The above experiments showed that the shape of the pulses generated by this multivibrator was not ideal. If however the pulse size is constant for a given combination of R_1, R_2, C_1 and C_2, then the multivibrator could be used to electrogenerate

a constant quantity of bromine with every pulse. The most direct method for testing the constancy of the pulse size obtained with this type of multivibrator is to electrodeposit silver or copper in a coulometer as described in the experimental section.

Twenty-five sets of data were obtained for the electrodeposition of silver and about twenty for copper. In the former case the time allowed for the electrodeposition was exactly 30 min, and the number of pulses registered for this period and the weight of the silver deposited were measured. Because copper has a small electrochemical equivalent, the time for the electrodeposition was increased to 60 min in order to get an appreciable deposit of copper. The results were analyzed statistically and the standard deviations are shown in Table II. The pulse size, calculated from the amount of silver deposited varies between $7.47 \cdot 10^{-3}$ and $7.57 \cdot 10^{-3}$ coulombs/pulse; when calculated from the amount of copper deposited, the pulse size is found to vary between $5.75 \cdot 10^{-3}$ and $5.96 \cdot 10^{-3}$ coulombs/pulse. The low result obtained for the pulse size from the electrodeposition of copper can be readily explained. The electrodeposited copper redissolves in the electrolyte during the time interval in which no current is passing through the coulometer, *i.e.*, during the time interval between two pulses. This reduces the total weight of copper electrodeposited and thereby gives rise to a smaller pulse size. The tendency for silver to redissolve in the electrolyte in this manner is small.

Table II shows the effect of using new tubes in the multivibrator circuit. On replacing the aged tubes with new ones, there was a considerable change in the pulse size.

In all electrodeposition experiments carried out under a variety of conditions, it was noticed that the deposits of silver and copper were crystalline and it would seem that the use of current pulses to electrodeposit metals, favors the formation of crystalline deposits.

The indicator electrode system

The pulse and counting circuits shown in Fig. 1 were used for the electrogeneration of bromine. Two indicator electrode systems were examined in this work, a platinum macroelectrode of area 5.38 cm^2 and a rotating platinum microelectrode. The optimum polarizing voltage that should be used with platinum electrode systems in solutions containing bromine and bromide ions, was first established. Polarizing voltages between $+0.62$ V and $+0.22$ V *vs.* the reference saturated calomel electrode, fall on the limiting current plateau of the current–voltage curve, obtained for the electroreduction of bromine to bromide ions at the platinum electrode. All polarizing voltages used in our experiments were within this optimum range.

In order to evaluate the response of the platinum macroelectrode to $Br^- - Br_2$ in solution, bromine was electrogenerated in solutions each containing 25 ml 0.5 M KBr and 25 ml 0.1 M HCl. After the generation of a definite amount of bromine, the current in this indicator circuit decreased continuously with time. If each current reading was taken at a definite time, say 15 sec after the electrogeneration of bromine was interrupted, plots of current against number of pulses could be obtained. Except for a slight initial curvature, these plots were linear. However their slopes were different for different modes of pretreatment of the platinum electrodes, and these slopes were not reproducible. Consequently variable titration blanks, from 0.3 to 6.0 pulses, were obtained.

When a platinum macroelectrode was employed as the indicator electrode, the current in the indicator circuit showed a decrease of 5.2 μA in 40 min, after a definite quantity of bromine was electrogenerated with 21 pulses. A similar experiment was carried out with a rotating platinum microelectrode; the same amount of bromine was electrogenerated (21 pulses) and the current in the indicator circuit showed a decrease of only 0.7 μA in 40 min. Furthermore, with a rotating platinum micro-electrode, reproducible plots of the number of pulses vs. current in the indicator circuit, were obtained and the titration blanks were negligibly small. Hence, the rotating platinum microelectrode is much more satisfactory as an indicator electrode for the amperometric determination of bromine in spite of the fact that it has a lower sensitivity than the platinum electrode with a large surface area. In all bromometric titrations described in this work, the indicator electrode consisted of a rotating platinum microelectrode.

The condition of the surface of the platinum indicator electrode was an important factor which determined the precision and accuracy of coulometric titrations with electrogenerated bromine. The rotating platinum microelectrode in the indicator circuit as well as the platinum generator electrode in the bromine generating circuit were pretreated before every experiment by a method described by KOLTHOFF AND TANAKA[2]. An oxide film was first formed on the platinum surface when the electrode was immersed in concentrated nitric acid. The electrode was then washed thoroughly with distilled water and the oxide film reduced by placing the electrodes in a solution of ferrous sulfate. Finally, the electrodes were rinsed with distilled water and placed in the central compartment of the titration cell. The use of this pretreated electrode in the amperometric circuit for detecting the end-point in the bromometric titration of 8-quinolinol and arsenic(III), gave reproducible titration curves. Furthermore, titrations which were carried out in which the 8-quinolinol or As(III) were omitted, gave negligible blanks.

TABLE III

TITRATION OF 8-QUINOLINOL WITH ELECTROGENERATED BROMINE

$B + = 250$ V; $R_1 : R_2 = 1$ MΩ : 1 MΩ

μg 8-quinolinol	No. of pulses	No. of pulses per μg of 8-quinolinol
500	455	0.910
400	367	0.918
300	272	0.907
250	232	0.928
200	183	0.915
150	139	0.927
100	99	0.990
50	49	0.980
40	39	0.975
20	21	1.050
$B + = 200$ V : $R_1 : R_2 = 100$ KΩ : 100 KΩ		
500	3750	7.500
450	3406	7.569
350	2636	7.531
250	1886	7.544
200	1510	7.550
150	1137	7.580
50	400	8.000

Titration of 8-quinolinol

The central compartment of the titration cell contained 50 ml of solution which was made up as follows: 25 ml 0.5 M KBr, x ml of a standard solution of 8-quinolinol in 0.1 M HCl and (25—x) ml of 0.1 M HCl. In the multivibrator circuit $B+ = 250$ V and $R_1 : R_2 = 1$ MΩ : 1 MΩ. A second set of results was obtained when $B+ = 200$ V and $R_1 : R_2 = 100$ KΩ : 100 KΩ. An R.C.A. microammeter and a pretreated rotating platinum microelectrode were used in the indicator circuit. All current readings in the indicator circuit were taken 2 min after the interruption of the bromine generation since it was found that the current reached a steady value after this time interval had elapsed. The results obtained are given in Table III.

Titration of arsenic(III)

A solution containing As(III) was made up as follows: 15 ml 0.5 M KBr, 25 ml 1 M H$_2$SO$_4$ and the standard As(III) solution, made up to a volume of 50 ml. The multivibrator settings were $B+ = 200$ V and $R_1 : R_2 = 100$ KΩ : 100 KΩ. The experimental technique employed was the same as that for the titration of 8-quinolinol, and the results obtained are shown in Table IV.

TABLE IV
TITRATION OF ARSENIC(III) WITH ELECTROGENERATED BROMINE
$B+ = 200$ V; $R_1 : R_2 = 100$ KΩ : 100 KΩ

μg arsenic(III)	No. of pulses	No. of pulses per μg arsenic(III)
300	2177	7.257
180	1306	7.256
120	873	7.275
8.4	609	7.250
60	450	7.500
36	270	7.500
24	182	7.583

DISCUSSION

The attempts to determine the pulse size electrogravimetrically, using a copper coulometer, were unsuccessful since a certain amount of the electrodeposited copper redissolved in the electrolyte during a run. With a silver coulometer the pulse size, calculated from the results in Table II, is 8.507 $\pm$ 0.107 μg/pulse. Therefore, the percentage error is 1.26%, which is identical with the percentage error for the weight of the silver electrodeposited, when the time is kept constant. Since the percentage error in the pulse rate is 0.5%, it is reasonable to assume that the pulse size also is subject to the same percentage error. However, the observed percentage error for the pulse size is 2.5 times the expected error. This increased error may be due to a number of factors. The nature of the deposits formed was not ideal and considerable difficulties were involved in collecting, washing and drying these granular or crystalline deposits. It is also possible, just as in the case of copper, for the electrodeposited silver to redissolve in the electrolyte during the electrodeposition. A variation in the pulse size could also be caused by a variation in the voltage supplied by the power pack over a long period of time or a change in the tube characteristics in the multi-

vibrator. The results in Table II show that the pulse size is dependent on the "age" of the tubes. If the "aged" tubes were replaced with new ones, the pulse size showed a considerable change.

It must be emphasized that most of the errors that have been mentioned are encountered on examining the long term stability of the instrument. The short term reproducibility of the pulse size is considerably better than 1%. For maximum accuracy and reproducibility, the pulse size should be calibrated with a standard solution of the substance to be titrated, before a series of determinations is carried out.

The pulse size obtained from the instrument, described in the first part of the experimental section and shown in Fig. 1, was determined by a number of methods. When $B+ = 250$ V and $R_1:R_2 = 1$ MΩ : 1 MΩ a silver coulometer gave a pulse size of $3.25 \cdot 10^{-3}$ coulombs/pulse. When a standard solution of 8-quinolinol was titrated using the same experimental conditions, the pulse size was found to be $2.92 \cdot 10^{-3}$ coulombs/pulse. When $B+ = 200$ V and $R_1:R_2 = 100$ KΩ : 100 KΩ the pulse size obtained by titrating a standard solution of 8-quinolinol was $3.54 \cdot 10^{-4}$ coulombs/pulse. If a standard solution of arsenic(III) was used, the pulse size was found to be $3.55 \cdot 10^{-4}$ coulombs/pulse. Therefore, in the titration of 8-quinolinol and arsenic(III) with electrogenerated bromine, the titration efficiency is 100%, under the experimental conditions used.

It is evident from this work that the direct determination of the pulse size using a silver coulometer is unreliable for reasons that have already been mentioned. Our results indicate that the electrogeneration of bromine is 100% efficient and the titration efficiency is 100% in the bromometric titration of 8-quinolinol and arsenic-(III). However, Tables III and IV show that in order to titrate less than about 100 μg of 8-quinolinol, an excess of electrogenerated bromine is required. This effect has been reported previously[1] and confirmed repeatedly in this work. In the titration of arsenic-(III) an increased quantity of bromine was required for the titration of quantities less than about 100 μg arsenic(III). The reason for this anomalous behavior is under investigation.

SUMMARY

A simplified multivibrator circuit has been constructed and the suitability of this simplified circuit for coulometric titrations has been investigated. The factors that affect the coulombic magnitude as well as the rate of generation of current pulses, have been evaluated. Arsenic(III) and 8-quinolinol have been titrated with electrogenerated bromine and a pretreated rotating platinum microelectrode has been shown to be the most suitable indicator electrode for detecting the end-point in these titrations.

REFERENCES

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2 I. M. KOLTHOFF AND N. TANAKA, Anal. Chem., 26 (1954) 632.