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Digitally Controlled Automatic Coulometric Karl Fischer Titrator

Kisaburo UMEMOTO
Department of Pure and Applied Sciences, College of General Education, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153

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An automatic coulometric Karl Fischer titrator capable of direct readout of the water titrated and the background of titration was constructed. Control of the generation of reagent was carried out by a digital counting method. The over- and under-titration was minimized by holding the level of reagent at the start and the end of titration as close as possible. Details of the circuit configuration were presented. The precision of determination was *ca.* ±2 μg and ±1—±2 μg for the automatic titration of 1 mg and 10—500 μg of water, respectively. Water of less than 20 μg was titrated within a precision of 1 μg by watching the drift and subsequent recovery of the blank level.

Karl Fischer determination of water is based on a reaction in which 1 mol of iodine is consumed in the titration of 1 mol of water in a methanolic solution of pyridine, sulfur dioxide and iodine. In the coulometric determination of water, iodine is generated by electrolysis and the amount of water is determined by measuring the quantity of the current consumed during titration, since 10.71 mC is required for each microgram of water.1) At the end point of titration excess iodine is generated, which is detected by the depolarization of platinum indicator electrodes. The coulometric Karl Fischer titration was found to be suitable for the determination of a trace of water.1–12) For the purpose to automate the titration, Kelly *et al.* designed an automatic cutoff attachment to a pH meter2) but the current for compensating the background of titration was set manually. Hoyt constructed an automatic end point indicator7) but no care was taken for compensation of the background of titration. Miyake and Sudo constructed an instrument capable of automatic control of the generation of iodine and also capable of automatic elimination of the blank,12) but compensation of the background of titration was not performed. Recently, automatic coulometric Karl Fischer titrators capable of automatic compensation of the background of titration have appeared.17,18) The electrolysis current of Mitsubishi Kasei Model CA-02 titrator is controlled to be proportional to the drift of the potential of the indicator electrodes, the titration being terminated when the electrolysis current substantially returns to the blank level. However, insufficient period of time for anticipation of the end point restricts the accuracy of determination of a micro amount of water, since the Karl Fischer reaction is not fast enough to assure the instant completion of reaction.14–16) Hiranuma Sangyo Model AQ-3B titrator was constructed on the basis of constant current coulometry; near the end of titration the current is periodically interrupted with subsequent anticipation of the end point. In the method of anticipation of the end point, some overshoot at the end point is present since the end point is determined when the potential of the indicator electrodes lasts above the cutoff potential over a given anticipated period of time. No care has been taken for minimizing this type of over-titration except for restricting the generation of iodine near the end point. Moreover, in constant current coulometry, inaccuracy in the count of current was caused by the switching time delay in each on-off operation of the electrolysis current.12)

The automatic coulometric Karl Fischer titrator presented in this paper was designed with the following improvements. (i) The electrolysis current is so adjusted that 100% current efficiency is guaranteed for any size of working electrode and concentration of the reagent. The current was measured by current-to-frequency conversion with subsequent counting for integration. (ii) The method of anticipation of end point is preferred in order to avoid the risk of under-titration since the Karl Fischer reaction is not instantaneous in spite of much improvement in the reagents.13–16) Care was taken to minimize the overshoot at the end point not only by restricting the rate of generation of iodine near the end point but also by holding the potential of the indicator electrodes at the start and the end of titration as close as possible. (iii) With the use of digitally controlled counting method of the blank, the waving drift in the level of iodine during the standby state12) is minimized by controlling the generation of iodine to one count for each detection of the blank. (iv) The background of titration is directly read out by integrating the level of the blank instead of compensating it. This method is more simple than the method of compensation since no extra precise control of the constant current power supply is required. (v) The blank level is directly read out so that micro amount of water can be accurately determined by watching the drift and the subsequent recovery of the blank level.

Apparatus

A block diagram of the instrument is shown in Fig. 1. The blank level is held prior to introduction of the sample in order to integrate it for counting the background of titration. After introduction of the sample, electrolysis is started by opening the gate of the transistor switching circuit. The electrolysis current is fed into the current measuring circuit and converted into the frequency of one count equivalent to one microgram of water, the count being read out on the display unit. The background counting circuit integrates the blank level until the end of titration is reached, the count being read out on another display unit. The monitoring circuit detects any excess or deficiency of iodine, giving out "on" and "off" signals for controlling the electrolysis. The end point determining circuit detects the approach of end of titration; near the end point the amount of generating iodine is restricted by the controlling circuit. At the end point of titration, the controlling circuit starts to control the counting of the blank and holding of the blank level. During this standby state for subsequent titration, the blank level can be read out on the diplay unit with the operation of the selection switch. Details of the circuit configurations are given below, where all the TTL logic gates are composed of SN74LS series and the power supplies are regulated by the standard method.

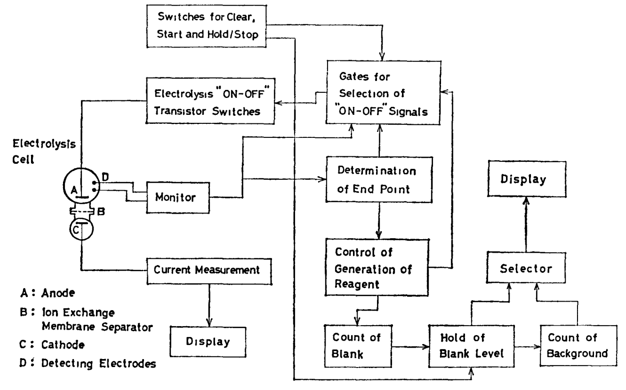

Fig. 1. Block diagram of the functional construction of the instrument.

Operation for Start, Hold/Stop, and Clear. The circuit is shown in Fig. 2. The whole circuit is reset by signal *a* from gate G_1; automatically by a delay circuit when power is switched on or manually by pushing spring switch S_1. When spring switch S_2 is pushed to "Hold/Stop" position, latch L_1 is reset to stop the electrolysis. This operation is performed prior to introduction of the sample. In order to start titration, switch S_2 is pushed to "Start" position, triggering timer T_1 to give a pulse *c* which resets the results of the previous titration. At the end of pulse *c*, latch L_1 is set to activate gate G_3 to start electrolysis. The electrolysis current power supply is adjustable in the range 5—25 V.

Monitoring Circuit. A potential difference of a few millivolts is given between the detecting electrodes (Fig. 2). When excess water is present in the cell, the cathode of the detecting electrodes is polarized, no current flowing. However, when iodine is in excess the cathode is depolarized and a small current flows, resulting in a voltage drop across a resistor of 1 kΩ. The voltage drop is fed into operational amplifier A_1. The noise involved in the voltage due to the turbulent mixing of the solution is substantially filtered off by placing a capacitor in the feedback loop of A_1. A_1 is balanced *ab initio* so that its output is nega-

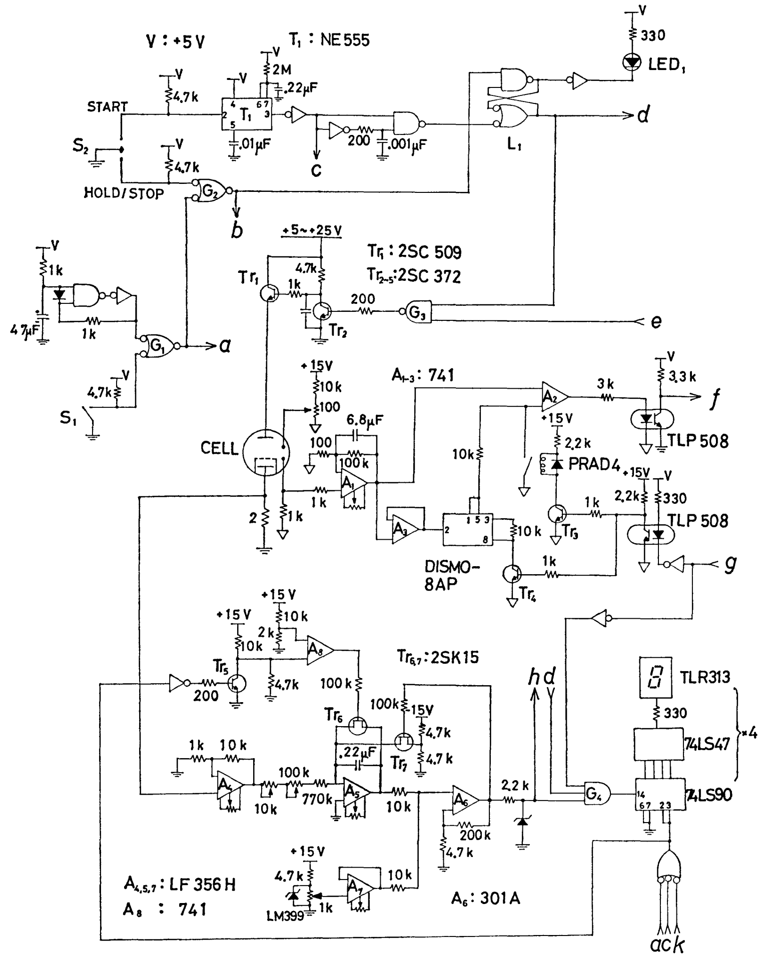

Fig. 2. Operational, monitoring, and current measuring circuits.

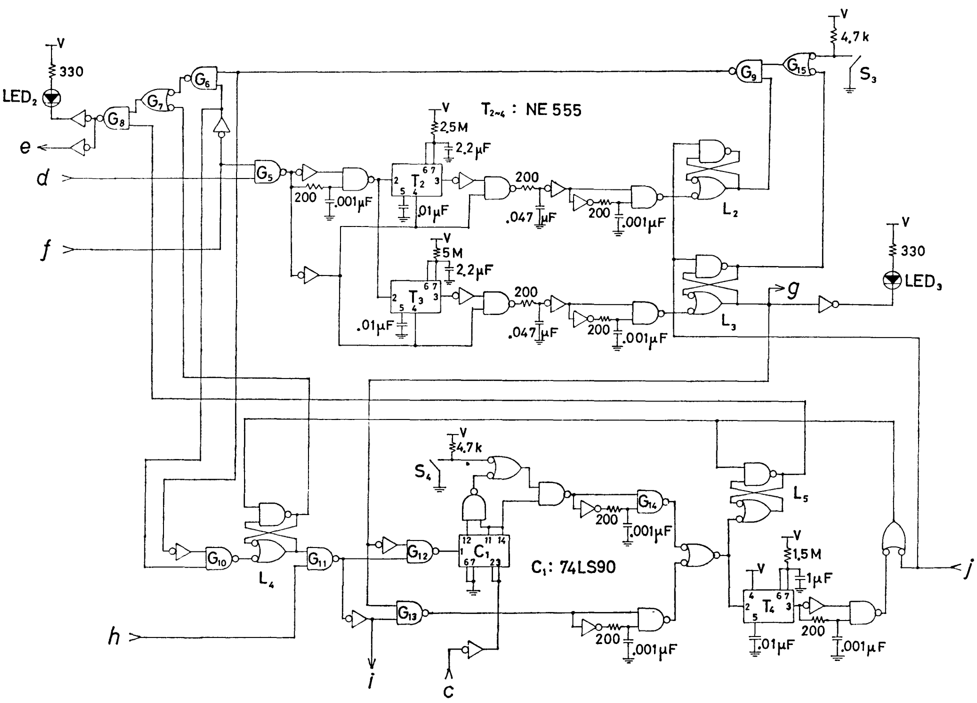

Fig. 3. End point determining and controlling circuits.

tive when excess water is present in the cell. The output of A_1 increases as the titration approaches the end point, turning to positive when excess iodine is detected. The output of A_1 is fed into comparator A_2 which is used as a zero cross detector during the course of titration. The output of A_2 is fed into a photocoupler whose output signal *f* controls the "on" or "off" of the electrolysis depending on whether iodine is deficient or excess in the cell. Isolation of the monitoring circuit is necessary for the electrolysis cell current not to flow into it. The monitoring circuit is operated with an isolated power supply.

The sample-hold circuit DISMO 8AP(Xebec) was used to minimize the overshoot at the end point. At the end point of each titration, the potential of the detecting electrodes was found to concentrate around a potential which is a little higher than zero, indicating that the amount of excess iodine present at the end point of titration is about the same for each titration. The overshoot at the end point is minimized by starting subsequent titration from this level of excess iodine to make the level of iodine at the start and the end of titration as close as possible. In order to maintain this level of excess iodine constant during the standby state, the cutoff potential of the monitoring circuit is switched from zero to a potential which is held by the sample-hold circuit DISMO 8AP at the end point of titration.

Current Measuring Circuit. The current through the cell is measured with a voltage drop across a high quality precision resistor of 2 Ω and converted into frequency with a V-F converting circuit (Fig. 2). High quality metal film resistors and a polycarbonate capacitor were used to ensure the accuracy and stability of this circuit. The time required for resetting the integrator was *ca.* 15 μs. The integrator was so adjusted that the V-F converter advances one count within an accuracy of 0.1% on flowing a current of 10.71 mC through the current measuring resistor and the amount of water titrated is directly read out in microgram unit. The output of the V-F converter is fed into the counter of the display unit *via* gate G_4 which is opened by the start signal *d* and closed by the end point signal *g* to register the result of the titration.

End Point Determining and Controlling Circuit. The end point determining circuit and the controlling circuit are shown in Fig. 3. At an early stage of titration, the signal *f* passes through gates G_6, G_7, and G_8, and controls the "on-off" of the electrolysis. On approaching the end point, the rate of generation of iodine exceeds that of consumption and the electrolysis stops temporarily. The excess iodine is soon consumed by the residual water, electrolysis starting again. This procedure is repeated, the interval of "on" being elongated with approach to the end point. Titration has been completed to 98—99% and to 100% when the electrolysis "off" continues for 8 and 20 s, respectively. Timers T_2 and T_3 are used to detect the approach or reach of the end point, each delay time being determined as 8 and 20 s, respectively. Both timers are triggered at the instant the signal *f* turns to "off" and reset when *f* turns to "on" before each delay time is over. When the electrolysis "off" begins to last over 8 s, latch L_2 is set and signal *f* is introduced into the controlling circuit *via* gate G_{10} so that the subsequent electrolysis is controlled at gates G_7 and G_8 by latches L_4 and L_5. When signal *f* turns to "on," L_4 is set to make the electrolysis "on," and the current counting pulse *h* is fed into the counter C_1 *via* gates G_{11} and G_{12}. The outputs of C_1 are wired into a scaler so that L_5 is set to stop the electrolysis at 5 or 10 counts advance depending on whether preset switch S_4 is open or closed. Timer T_4 is used

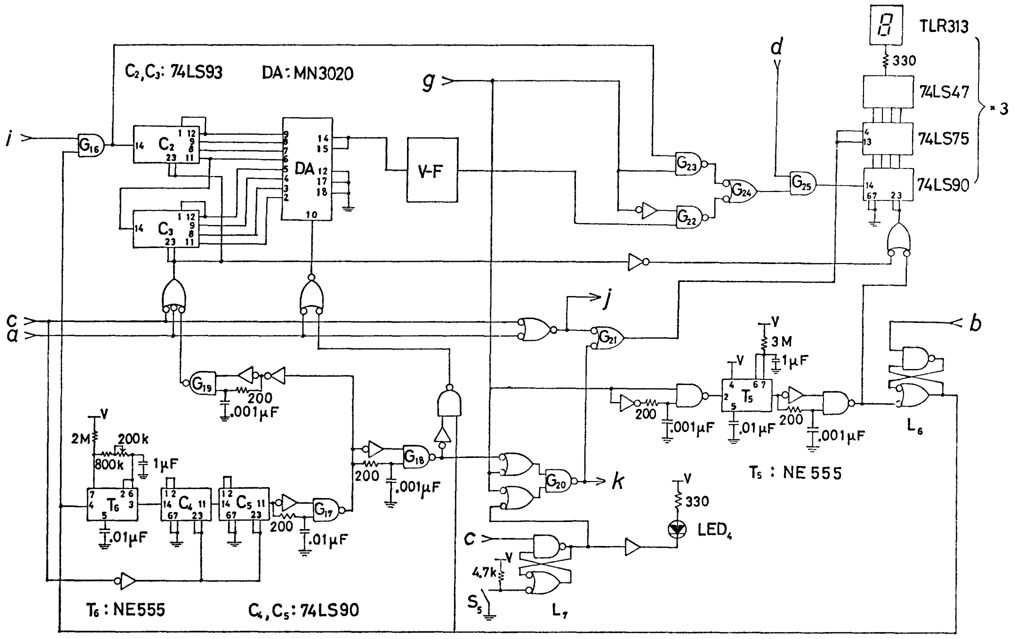

Fig. 4. Circuits for counting the blank, holding the blank level, and counting the background of the titration.

to provide a time delay of about 1.2 s before the reset of L_4 and L_5 to ensure the generated iodine to reach the detecting electrodes. Generation of a preset amount of iodine and subsequent waiting is repeated whenever the signal *f* turns to "on" until the end point of titration is reached. When the electrolysis "off" lasts over 20 s, latch L_3 is set to stop titration. With the signal *g*, gates for counting the electrolysis current and the background of titration are closed, DISMO being switched to "hold" mode and counting of the blank is started.

Circuits for Counting the Blank and Holding the Blank Level. The circuit for compensating the blank is shown in Fig. 3. The signal *g* closes gate G_{12} and opens gate G_{13} at the end of titration, the rate of generating iodine being restricted to one count whenever the blank is detected. The waving drift in the level of iodine[12] is minimized at most to one count during the standby state.

The blank level is defined as the number of blank for 30 s and determined by counting the blank current counting pulse *i* by a controlling method as shown in Fig. 4. The pulse *i* is fed into gate G_{16} which is activated at 5 s after the end of titration with latch L_6 and timer T_5. The delay is required for waiting for the cutoff operation of the monitoring circuit to settle at a voltage held by DISMO 8AP. When L_6 is set, G_{16} is opened for introducing *i* into counters C_2 and C_3, oscillator T_6 being activated simultaneously. T_6 is *ab initio* adjusted so that pulses with 30 s interval are obtained from G_{17}. From the leading and trailing edge of this pulse, non-overlapping pulses are obtained from gates G_{18} and G_{19}. The pulse from G_{18} registers the count of C_2 and C_3 into the D/A converter, and the pulse from G_{19} clears the counters. In this manner, the counters count the numbers of the blank and transfer it to the D/A converter before being cleared at every 30 s to hold the latest blank level.

In parallel with these operation, the blank is also counted with the BCD counters of the display unit. When the blank level is required to be displayed, spring switch S_5 is pushed to set latch L_7, which opens gate G_{20} so that the pulse from G_{18} is given to the shift registers as a strobe to show the blank level.

Circuit for Counting the Background of Titration. The background of titration is counted by integrating the blank level held just before the start of titration. The circuit for counting the background of titration is shown in Fig. 4. By pushing switch S_2 to "Hold/Stop" position (Fig. 2), latch L_6 is reset by signal *b* to make gate G_{16} and oscillator T_6 inactive so that the D/A converter continues to hold the last blank level until the end of titration is reached. The output of the D/A converter is fed into a V-F converter consisting of the same circuit configuration as that used in the electrolysis current measuring circuit. The time constant of the V-F converter is *ab initio* adjusted so that the counting rate coincides with the blank level. The output of the V-F converter is fed into BCD counters through gates G_{22}, G_{24}, and G_{25}. The shift registers of the display unit are kept active while titration proceeds, but made inactive by signal *g* to keep the counted background of titration on the display unit after the end of titration. The count of the background of titration is subtracted from the reading of the electrolysis current to obtain the net amount of water titrated.

Experimental

Aqualyte G (generator electrolyte) and aqualyte C (counter electrolyte) from Hiranuma Sangyo were used as Karl Fischer reagent. The water–methanol solution was prepared by diluting 247.0 mg of water with dehydrated methanol in a measuring flask of 25.00 ml calibrated by weighing pure water. The density of pure water was taken into consideration for calibration. The water content in the methanol taken in the measuring flask was determined to be 0.440 mg/ml. The water content in the water–methanol solution was calculated to be 10.32 mg/ml. The solution was transferred into a sample bottle in a dry bag and sealed with a serum-type rubber stopper. The water–methanol solution was taken with a 100 µl(# 710) or 10 µl(# 701) Hamilton micro syringe which has an accuracy of 1% full scale. The titration vessel was a separable H-type cell with an assembly similar to that reported.[1,13]

Results and Discussion

In order to examine the effect of the rate of iodine generation, the voltage applied to electrolysis was changed in the range 5—25 V. The corresponding rate of iodine generation was 3—18 counts/s, for which the titration of a given amount of water gave an identical result. This indicates that the condition of 100% current efficiency is preserved in this range of applied voltage. The voltage for the routine use was adjusted to approximately 15 V in order to limit the rate of iodine generation to *ca.* 10 counts/s, sufficiently lower than the safety limit. Incomplete titration was avoided by confirming that the blank level returned to the original level at the end of titration.

Accuracy and precision of titration is affected by the stability of the blank level. If the blank level is not settled, error is caused in the counting of the background of titration. When a fine porosity glass filter was used as a separator of the two compartments of the titration vessel, the blank level was high and unstable. The blank level increases after each titration unless the level of the counter electrolyte is kept lower than that of the generating electrolyte. This indicates that use of this type of separator is restricted by the leakage of counter electrolyte. When an ion-exchange membrane[12] was used as separator, the blank level was kept low and stable. The following determinations were carried out with an ion-exchange membrane as separator.

The results of titration of the standard water-methanol solution are given in Table 1. The precision was *ca.* ±2 µg and ±1—±2 µg for automatic titration of 1 mg and 10—500 µg of water, respectively. The time needed for the titration of 1 mg of water was *ca.* 150 s. The precision is better than that reported for the automatic coulometric Karl Fischer titrator.

The over- and under-titration was minimized by holding the level of iodine at the start and the end of titration as close as possible by using a sample-hold circuit (Fig. 2). The waving drift in the level of iodine during the standby state was minimized by restricting the rate of iodine generation to one count for each detection of the blank level by digitally controlled counting method (Fig. 3). The effect of these circuit devices was examined as follows.

When a small amount of water is introduced into the cell, the reading of the blank level increases but it soon returns to the original level. The amount of water is determined by taking the summation of the differences obtained by subtracting the original blank level from those read out at 30 s intervals. Over- or under-titration is thus completely avoided. The results are given in Table 2. The amount of water less than 50 µg was determined with a precision of ±1 µg. By comparing the results shown in Tables 1b) and 2, the average values were found to agree within an accuracy of 1 µg, indicating that the error due to over- or under-titration does not exceed 1 µg.

An example showing absolute accuracy of the method of determination of water by watching the drift and subsequent recovery of the blank level was given for the determination of atmospheric humidity. Air was taken with a 1 ml tuberculin syringe. The results are given in Table 3. The experimentally obtained values agree with the values calculated from the relative humidity within an accuracy of 1 µg with a preci-

TABLE 1. REPEADABILITY OF TITRATION OF WATER–METHAL SOLUTION (10.32 mg H_2O/ml)

Amount of sample µl	No. of runs	Found µg
a) Sample taken with 100 µl micro syringe.		
100	7	1035.6±1.9
50	7	520.4±1.7
10	5	109.6±1.0
b) Sample taken with 10 µl micro syringe.		
10	5	104.2±1.9
5	6	52.0±1.7
2	5	22.2±1.5
1	5	11.2±1.5

TABLE 2. REPEADABILITY OF TITRATION OF WATER–METHANOL SOLUTION (10.32 mg H_2O/ml)[a]

Amount of sample µl	No. of runs	Found µg
5	6	52.1±1.0
2	6	22.2±1.0
1	6	11.4±0.8

a) The end point of titration was determined by watching the drift and subsequent recovery of the blank level. Sample was taken with 10 µl micro syringe.

TABLE 3. DETERMINATION OF WATER CONTENT IN 1.0 ml OF ATMOSPHERIC AIR

Temperature °C	Relative humidity %	No. of runs	Found µg	Calculated µg
23.8	53	12	11.1±0.4	11.7
24.0	70	10	15.7±0.8	15.3
23.0	23	8	5.9±0.7	5.4

sion of less than ±1 μg. The discrepancy observed in the titration of 10 μl of the standard water–methanol solution taken with different micro syringes (Table 1) is due to the inaccuracy in the scale of the micro syringe.

In conclusion, the circuit devices presented in this work are useful for improving the accuracy and precision of the automatic coulometric Karl Fischer titration of water.

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