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Electronics is an important topic in chemistry courses, since most instruments employed by chemists involve electronic components in their construction and operation. Understanding of some fundamental concepts helps to comprehend how modern instruments work, enabling students to recognize their advantages and limitations. Frequently, new devices necessary for characterizing chemical systems need to be developed by chemists themselves and some knowledge of electronics allows chemists to get additional information from an expert. The importance of teaching basic concepts in electronics is evident in modern analytical chemistry. Nevertheless, teaching electronics is troublesome in chemistry courses, and several authors have suggested valuable ways to incorporate these topics in instrumental analysis courses (*1–4*). In this work, we propose the construction of a simple and inexpensive device, a photometric titrator, that is useful to demonstrate some basic concepts in electronics, showing its importance to modern analytical chemistry.

Some simple instruments frequently used in analytical labs, such as spectrophotometers, can sometimes be seen as “black boxes” by the students. It is therefore useful to know some basic electronics, as common electronic devices can be employed to build simple instruments that can be used for analytical measurements. In addition, some important classical procedures (titrimetry, for example) might become more interesting by association with simple electronic circuits. This can be adequately stressed by means of demonstrations or laboratory experiments.

Volumetric procedures (titrations) are among the oldest methods employed in analytical chemistry. Their uses include determination of physical chemistry parameters, such as equilibrium constants, and determination of concentrations by acid–base, redox, precipitation, or complexation reactions. Several procedures based on this kind of analysis are considered as standard or reference methods for the determination of a large number of substances (*5, 6*).

Titrations are based on the change of a physical property of the solution due to titrant addition. Concentrations are determined from the stoichiometry of the involved reactions and from the volume (or mass) of the titrant. The end point can be detected visually or by employing a sensor that responds to changes in the monitored property. Changes in the color of the solution are among the most frequently used strategies to find the end point of titrations. These changes can be followed visually or through photometric measurements. The latter is more suitable because it is less dependent on the perception of the analyst and the color of the samples has less influence. The fundamentals and some applications of photometric/spectrophotometric titrations have been presented (*7–10*).

However, special apparatus is necessary to perform titrations using conventional spectrophotometers, since it is necessary to stir the solution and to measure absorbance (or transmittance) after each addition of the titrant. Sometimes, these devices are not available in analytical teaching labs. Another drawback to performing spectrophotometric titrations is the time spent to complete the analysis, which can make the procedure tedious, especially when a large number of samples needs to be analyzed. An alternative is the use of automatic procedures to perform volumetric analysis.

According to definitions recommended by IUPAC (*11*), a procedure is considered automatic when at least one operation is controlled by a feedback system without human intervention. Feedback is defined as the use of the output of a device to modify the operation of an analytical instrument. In this sense, a titrator could be considered automatic if it is able to stop the addition of the titrant when the end point has been attained or to add an additional amount of the titrant if the change in the monitored property does not persist. Experiments with automatic equipment are described in some didactic articles (*12–14*), but automation is seldom employed according to IUPAC definitions.

This work proposes the construction of a simple low-cost apparatus (about US $150) to implement photometric titrations without a commercial spectrophotometer. The titrator is assembled employing a buret, a three-way solenoid valve, and electronic devices available commercially. It permits control of the addition of the titrant by switching the solenoid valve on or off until the end point is attained, as detected by a change in the color of the solution due to the presence of an indicator. A simple electronic circuit, which can be assembled by the students themselves, is employed to control the system. The assembly of the circuit is valuable to introduce to the students some fundamental topics in electronics that are useful in modern analytical chemistry. An automatic titration can be performed without control of a computer and terminology related to automation in analytical chemistry can be discussed. The experiment is also useful to emphasize the utility of the classical methods, such as volumetric analysis, that remain in use in laboratories of chemical analysis.

Construction of the Titrator

Apparatus

A three-way solenoid valve (model 161T031N, manufactured and supplied by NResearch) was employed in the construction of the photometric titrator. This is an electromechanical device usually employed to control flowing liquids or gases (*15*). Inside, these devices have a metallic moving

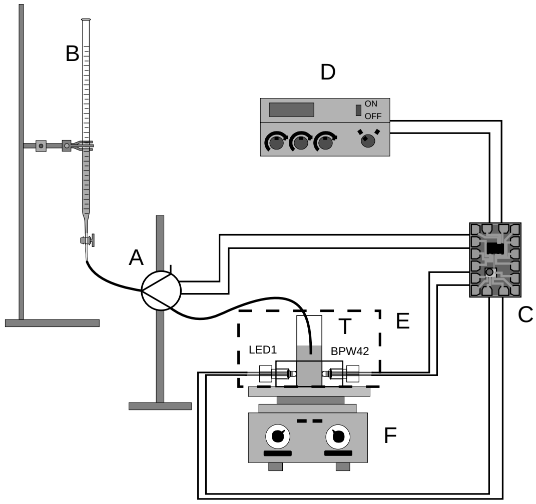

Figure 1. Schematic representation of the automatic photometric titrator. A: Three-way solenoid valve; B: buret; C: electronic circuit; D: bipolar 12-V power supply; E: part protected from ambient light; F: magnetic stirrer; T: titration vessel; LED1: light source; BPW42: photodetector.

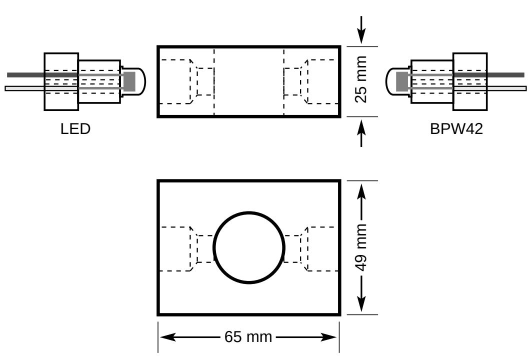

Figure 2. View of the perspex bloc used to align the light source (LED) with the phototransistor (BPW42) through the titration vessel.

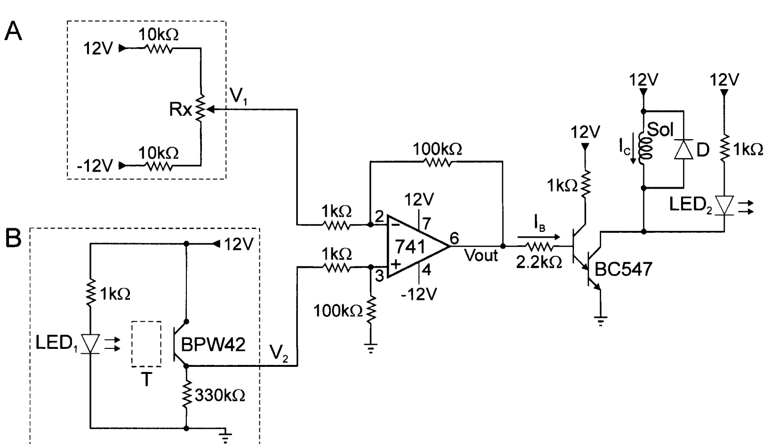

Figure 3. Schematic representation of the electronic circuit. A, B: voltage dividers; LED_1, LED_2: light-emitting diodes; BPW42: photodetector; T: titration vessel; Rx: variable resistor; 741: operational amplifier; Sol: inner solenoid of the valve; D: diode; BC547: transistor.

core and a solenoid. The valve is switched on by the passage of electric current (ca. 100 mA) through the solenoid, generating a magnetic field that displaces the core. There is a solution inlet and two outlets that are enabled when the valve is switched on or off. This device was coupled to a 10-mL buret to control the titrant stream.

The circuit was assembled employing electronic devices available commercially: one 741 operational amplifier (RS, stock number 428-385); two transistors (BC547; RS, stock number 296-087); resistors—1 kΩ (five), 2.2 kΩ (one), 10 kΩ (two), 100 kΩ (two), 330 kΩ (one), a 10-kΩ variable resistor (RS, stock number 375-691); one diode (1N4001; RS, stock number 261-148); and three light-emitting diodes (LEDs)—we used two green clear LEDs (Digi-Key, part number P302-ND) and a red clear LED (Digi-Key, part number P301-ND). A photometer was assembled with one LED (as light source) and a phototransistor BPW42 (as light detector), which were aligned in a perspex bloc. Other photodetectors (e.g., BPW 21; RS, stock number 303-719) could be used as well. A green and a red LED were used as light sources for the acid–base and redox titrations, respectively. The electronic circuit was fed by a bipolar 12-V power supply. Polyethylene tubes (0.8 mm i.d.) were employed to connect the solenoid valve to the buret and the titration vessel (a cylindrical tube, ca. 20 mm i.d.).

Description of the Titrator

The complete titrator, including the electronic circuit, can be assembled in a four-hour lab class. A schematic diagram of the titrator is shown in Figure 1. The three-way solenoid valve (A) is connected to the buret (B) and the titration vessel (T) by means of polyethylene tubes. The valve is linked to the electronic circuit (C) that is fed by a bipolar 12-V power supply (D). The titration vessel is inserted in the center of a perspex block constructed as shown in Figure 2. A light-emitting diode (LED) is aligned with the photodetector (BPW42) through the titration vessel (see Fig. 2). This part (Fig. 1, E) was protected from ambient light by using a dark perspex box and placed on a magnetic stirrer (Fig. 1, F).

The electronic circuit was constructed employing the wire wrap technique (*16*). Alternatively, breadboarding can be used by the students. This technique is faster and simpler than wire wrap, though it is not suitable for permanent circuits (*16*). A schematic representation of the circuit is shown in Figure 3. In the proposed assembly, there are two voltage dividers (A and B). The variable resistor (R_x) of the voltage divider A is used to change the voltage output (V_1). In the voltage divider B, the phototransistor (BPW42) causes changes in the output voltage (V_2) as a result of the light intensity that strikes it. The outputs of these dividers are connected to the inputs of the 741 operational amplifier (pins 2 and 3). This device is configured as a differential amplifier, so that the amplified output signal (V_{out}, pin 6) is proportional to the difference between the input signals (V_1 and V_2, pins 2 and 3, respectively), according to eq 1. Thus, the output of the operational amplifier (V_{out}) can be adjusted by changing the resistance of the variable resistor R_x.

$$V_{out} = [(V_1 - V_2)100\ k\Omega/1\ k\Omega] = 100(V_1 - V_2) \quad (1)$$

Transistors are usually employed as amplifying and switching devices, providing an output signal whose magnitude is proportional to the input signal (*17*). Two Darlington (*16*) transistors (BC547) are employed in the electronic circuit to provide the amplification of the current that is introduced in the base (I_B). This arrangement can be seen as a single transistor with the current gain equal to the product of the current gain of each transistor (β_1 and β_2). Thus, the current drained through the solenoid (I_C) is proportional to the current I_B:

$$I_C = \beta_1\beta_2 I_B \quad (2)$$

The transistors work as an on/off switch to the three-way solenoid valve. The current I_B (proportional to the output of the 741 operational amplifier, V_{out}) is amplified according to eq 2. When the current drained through the solenoid (I_C) reaches the threshold value (ca. 100 mA) the solenoid valve is switched on.

Initially, with the sample solution in the titration vessel, the maximum intensity of the light emitted by the LED1 strikes the phototransistor (BPW42). Thus, the difference of electric potential V_2 attains a maximum value. By means of the variable resistor R_x, the output of the voltage divider *A* (V_1) is changed. This allows adjustment of the output (V_{out}) of the 741 operational amplifier (see eq 1) in order to reduce the current I_B to a minimum threshold value required to switch the three-way solenoid valve (see eq 2). When this condition is attained, LED2 becomes bright, indicating that the solenoid valve was switched on and consequently the titrant solution flows through the buret. When the end point is achieved, the color of the solution changes and the light emitted by LED1 is partially absorbed. This reduces the light intensity that strikes the phototransistor BPW42, reducing the voltage V_2. Thus, there is a sharp reduction in the output of the 741 differential amplifier (V_{out}) and in the current I_B. The current through the solenoid (I_C) is decreased, switching the valve off and stopping the titrant addition. If the color of the solution does not persist, the light intensity that strikes the phototransistor BPW42 will increase; the solenoid valve will be switched on again, and the titrant will be added until the end point is achieved.

Reagents and Solutions

All solutions were prepared from analytical grade reagent in distilled and deionized water. Solutions containing from 5×10^{-4} to 1×10^{-2} mol L^{-1} HCl were prepared by dilution of a 0.10 mol L^{-1} stock solution. A sodium hydroxide solution (ca. 5×10^{-3} mol L^{-1}) was prepared from boiled water and a saturated (ca. 50% m/v) NaOH solution, to obtain a solution free of carbonate (*8*). A 1% m/v phenolphthalein solution (60% v/v ethanol) was used as acid–base indicator.

For iodimetric titration of ascorbic acid, a triiodide solution (0.03 mol L^{-1}) was freshly prepared from an acid solution (0.2 mol L^{-1} H_2SO_4) containing 0.01 mol L^{-1} potassium iodate (a primary standard) and 0.2 mol L^{-1} potassium iodide, according to eq 3 (*6–8*). The starch indicator was prepared by dissolving 0.20 g of soluble starch in 50 mL of boiling water. A mass of 0.5 g of each vitamin C tablet was dissolved in 100 mL of water.

$$IO_3^- + 8I^- + 6H^+ \rightarrow 3I_3^- + 3H_2O \quad (3)$$

Procedure

The titrator was constructed as described. For the acid–base titration, a green LED was employed as light source. A 5-mL aliquot of the HCl solution and 2–3 drops of the phenolphthalein indicator were added to the titration vessel. The polyethylene titrant delivery tube was inserted into the titration vessel and fixed above the light path with adhesive tape. The electronic circuit was adjusted to maintain the solenoid valve switched on while the solution remained colorless, by changing the resistance of the variable resistor Rx. When the color of the solution becomes pink, indicating a small excess of the titrant, the green light emitted by LED1 is absorbed, reducing the light intensity that reaches the phototransistor. The solenoid valve is switched off and this interrupts the titrant addition. The consumed titrant volume can then be determined by the students.

For the iodimetric titration of ascorbic acid, a red LED was used as light source to match the emission of the LED with the maximum absorption of the iodine–starch solution. A 5-mL sample of the vitamin C tablet solutions or 10 mL of filtered lemon juice was placed in the titration vessel with 2 mL of the starch indicator solution. The electronic circuit was adjusted as described for the acid–base titration. A 0.03 mol L^{-1} iodine solution was employed in the titration of the solutions of vitamin C tablets. A 10-fold dilution of this solution was required for the titration of lemon juice sample.

Results and Conclusions

The acid–base titration was performed with a green LED as light source, in order to match the radiation emitted by the LED1 (maximum emission intensity at 565 nm) with the maximum absorption of the phenolphthalein indicator (λ_{max} = 552 nm). Acid solutions were titrated with NaOH by employing the automatic titrator and a conventional titration procedure. The results obtained are shown in Table 1. The volume consumed in the automatic titration (V_{aut}) is correlated with volumes consumed by the conventional procedure (V_{conv}) by means of the equation

$$V_{aut} = 0.079 + 0.96V_{conv}; \qquad r = .9998 \quad (4)$$

Table 1. NaOH Consumed in Titrations of HCl Solutions

C_{HCl} / 10^{-3} mol L^{-1}	V_{NaOH} / mL[a]	
	Automated Method	Conventional Method
0.50	0.51 ± 0.04	0.51 ± 0.01
1.0	1.11 ± 0.02	1.07 ± 0.01
2.0	2.20 ± 0.03	2.07 ± 0.04
5.0	5.01 ± 0.01	5.21 ± 0.01
7.0	7.07 ± 0.01	7.30 ± 0.05
10.0	9.74 ± 0.05	10.0 ± 0.01

[a]Mean of 3 titrations ± uncertainty.

Table 2. Iodimetric Determination of Ascorbic Acid Concentration

Sample	Concentration of $C_6H_8O_6$ / g L^{-1a}	
	Automated Method	Conventional Method
Vitamin C tablet 1	4.96 ± 0.01	4.98 ± 0.02
Vitamin C tablet 2	4.32 ± 0.01	4.35 ± 0.01
Lemon juice	0.288 ± 0.001	0.288 ± 0.002

[a]Mean of 3 titrations ± uncertainty.

The paired *t*-test (*8*) showed no significant difference between the results at the 95% confidence level. A 0.7 % relative standard deviation was estimated by 10 replicates of the titration of a solution containing 5×10^{-3} mol L^{-1} HCl. As the end point of the titration can be found without human intervention, the procedure can be considered automatic according to IUPAC recommendations (*11*), even though the analyst participates in other steps of the process.

The automatic titrator was also used in the iodimetric determination (*7, 8*) of ascorbic acid in vitamin C tablets and lemon juice. A triiodide solution is employed as titrant and the I_3^- ion is reduced by ascorbic acid according to eq 5. Starch is employed as indicator, and the end point is detected by the deep blue color of the solution when a small excess of triiodide is added.

$$C_6H_8O_6 + I_3^- \rightarrow C_6H_6O_6 + 3\ I^- + 2\ H^+ \qquad (5)$$

A red LED (maximum emission intensity at 635 nm) was employed as light source (LED1, Fig. 1). The triiodide–starch solution shows 96% of the maximum absorption at this wavelength. The results attained by the automatic titration (Table 2) are in agreement with those obtained by the conventional procedure at a 95% confidence level.

These results indicate that good accuracy and precision can be obtained with a low-cost automatic titrator. Other volumetric procedures could be implemented with minor changes. LEDs emit visible radiation (red, yellow, green, and blue) over narrow wavelength ranges (ca. 30 nm). Thus, the light emitted by the LED1 (Fig. 1) must be reasonably matched with that absorbed by the indicator when the end point is achieved. In addition, the photodetector must be sensitive in the wavelength range of the light emitted by the LEDs. This was demonstrated by using different LEDs as light sources for the acid–base and redox titrations, which involve different color changes at the end point. If an unsuitable LED is used, an erroneous end point or none at all may be detected. However, the LED can be easily changed to allow other applications.

The construction of the titrator is useful to teach basic aspects of electronics such as Ohm's law, magnetic field generation, and voltage dividers. In addition, some devices usually employed in electronic circuits (resistors, diodes, LEDs, transistors, phototransistors, and operational amplifiers) can be presented to the students. A proper discussion of these concepts and the working of the devices is presented in the literature cited (*16–18*). The construction of an apparatus to implement a common procedure in chemical labs helps to introduce these concepts.

The use of LEDs and photodetectors is a suitable way to construct photometers (*19–21*). This could be discussed and a variation of this experiment could be useful to demonstrate this possibility.

The most common way to implement automatic procedures employs microcomputers. This has become more usual owing to the wide use of computers in laboratories. However, it is advisable to demonstrate that automatic procedures can be implemented without computer control or expensive instruments.

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