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Assembling and Using an LED-Based Detector To Monitor Absorbance Changes during Acid–Base Titrations

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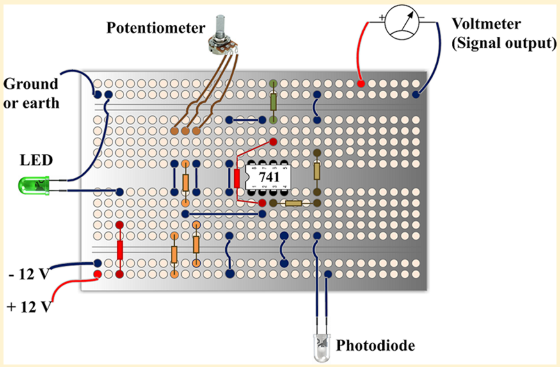
Supporting Information

ABSTRACT: A simple photometric assembly based in an LED as a light source and a photodiode as a detector is proposed in order to follow the absorbance changes as a function of the titrant volume added during the course of acid–base titrations in the presence of a suitable visual indicator. The simplicity and low cost of the electronic device allow the students to easily assemble the photometer and use it as a titration detector. The choice of the appropriate LED color should also demonstrate the principles of complementary colors. Concepts of data handling and relationship between the pH of the titration end point and indicator choice can be addressed. Errors associated with the use of wrong indicators can be demonstrated. The circuit assembly can highlight for the students the instrumentation and automation importance in modern chemical analysis. The discussion can be extended to relevant issues involved in this matter, such as light absorption, circuit analysis, and the hydrolysis concept, once they are involved and are closely related with the results obtained.



KEYWORDS: *Analytical Chemistry, Laboratory Instruction, Acids/Bases, Equilibrium, Applications of Chemistry, Instrumental Methods, UV-Vis Spectroscopy, General Public, Upper-Division Undergraduate, Continuing Education*

INTRODUCTION

Although instrumentation is an irreversible reality in chemical analysis, replacing the classical procedures, the instruments are becoming "black boxes" to the students, and even professionals, in analytical chemistry. Rarely the student of chemical courses has the opportunity of assembling and understanding how an instrument works. On the other hand, it is very important for the student to keep in mind that there are many chemical concepts behind an instrumental procedure.

Several papers on preparation and description of simple instrumental devices intended to be used for education purposes have been presented. Examples include the development of a digitizing circuit for measuring voltage with the Apple II game port,[1] conductivity devices,[2] and computer simulation of electronic circuits.[3,4] More sophisticated equipment intended to demonstrate principles of fluorimetry have been proposed by Bigger et al.[5]

LED-based devices were already proposed in the detection of amperometric end point by Spell and Philp, Jr., using equipment for the detection of the end point in the titration of cyclohexene with bromine.[6] However, it seems that the most focused subject concerning the use of LEDs is the assembling of photometric devices.[7,8] Wendlandt[9] proposed a colorimeter in which a green LED was the light source in order to minimize costs in teaching laboratories. Similarly, Dämmgen and Keune[10] used a standard light projector as a spectroscope, and Deldelumyea[11] proposed an LED-based device to demonstrate the principles of photometry with three basic experiments.

Hamilton and co-workers[8] prepared a low-cost, four-color LED photometer in which they suppressed the use of the optical components of a regular spectrophotometer by replacing them with LEDs. The device was evaluated by obtaining an analytical curve for $CuSO_4$ (Abs. vs C_{CuSO4}).

Reis and co-workers[12,13] proposed the use of a simple, low-cost apparatus that allows the automatic control of the titrant addition by switching a solenoid valve until the end point is attained. This is detected by the change in the color of the solution due to the presence of an indicator. An LED was used as the light source and a phototransistor was employed as the detector. The systems were used in the iodometric titration of ascorbic acid whose results agreed with those from the classical procedure.

Thal and Samide[14] described the construction of a simple spectrophotometer, in which a photodiode, a photoresistor, or a photodarlington were used as sensors and their performances were compared. Analytical curves for nickel, copper, and cobalt salts were obtained and revealed that the photodiode was the most sensitive detector.

In this work, a circuit to detect the end point in acid–base photometric titrations in the presence of a suitable indicator is proposed. The titration is performed by adding a standard basic

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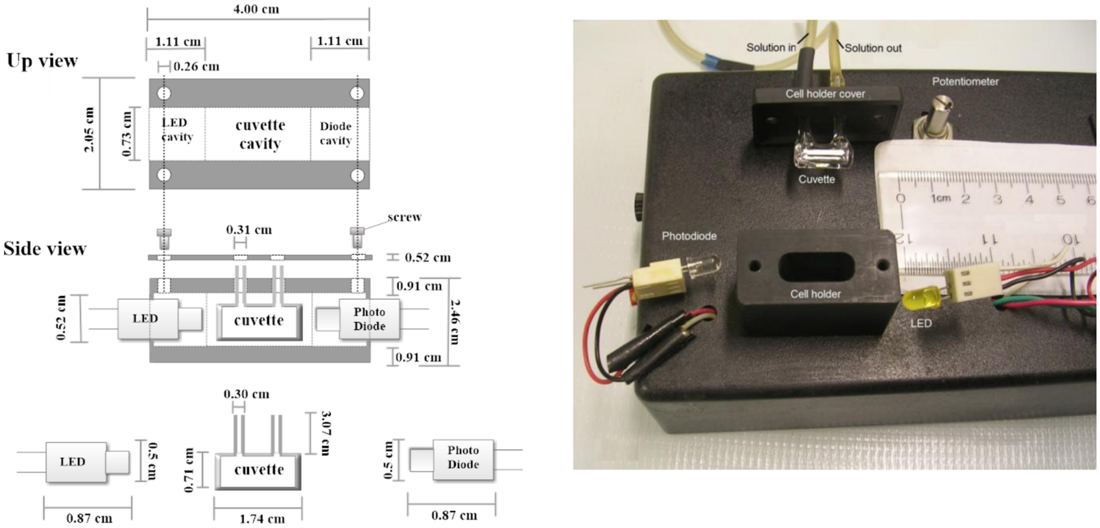

(a) (b)

Figure 1. (a) Schematic representation of the flow cell and details of the glass cuvette, LED and photodiode used in this work and (b) photography of the cell holder, cuvette, LED, and photodiode.

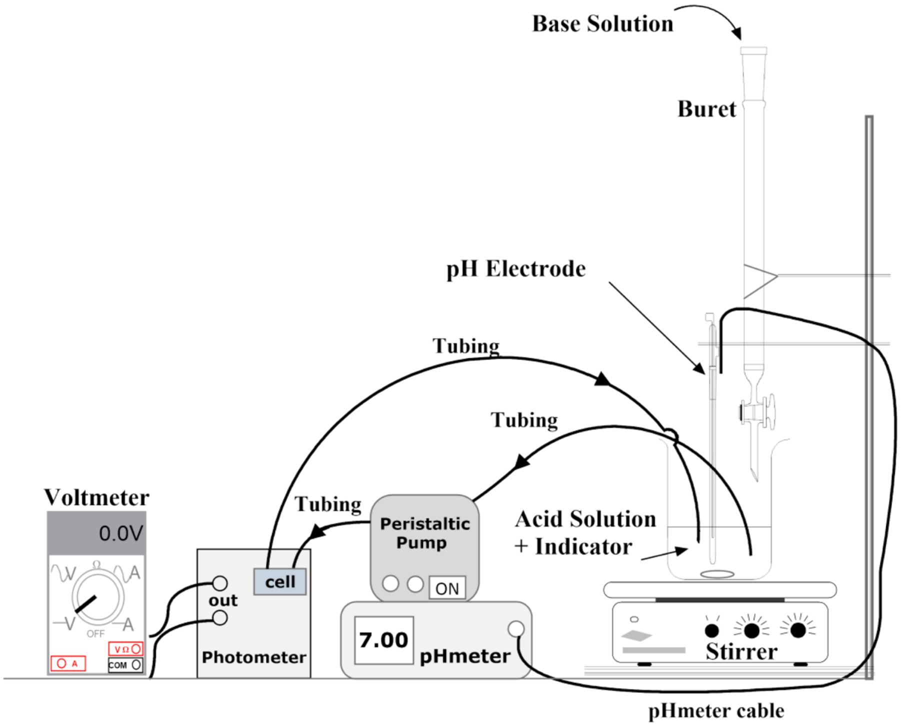

Figure 2. Experimental setup showing the titration vessel with the acidic solution, the buret from which the standard basic solution is added, the tubes that conduct the solution from the titration vessel to the photometer cell, with the help of a peristaltic pump, and the voltmeter that monitors the difference of electric potential generated by the photometer, based on the light intensity that reaches the phototransistor and the pH-meter to compare the results with the LED photometer. Figure inset shows details of the flow cell.

solution to the acidic sample, and the resulting color is monitored in an optical cell, in which the light from an LED interacts with the solution while it is measured with the help of a photodiode. A graph of electric potential difference from the detector as a function of the basic solution volume results in a sudden signal change when the color of the indicator changes in the end point. If the correct color of the LED is properly chosen, smaller errors in relation to the reference potentiometric procedure can be reached.

■ EXPERIMENT

Preparation of the Flow-Cell

The flow-cell holder was prepared in the house machine shop and was built in a black polyurethane block. Any other polymer that results in complete light blocking could be used. The flow-cell design is presented in Figure 1a, and consists of a main body with a hole to the flow glass cuvette and guides for the light source and the detector. A flow glass cuvette was prepared to fit inside the cell holder and with two solution guides on for

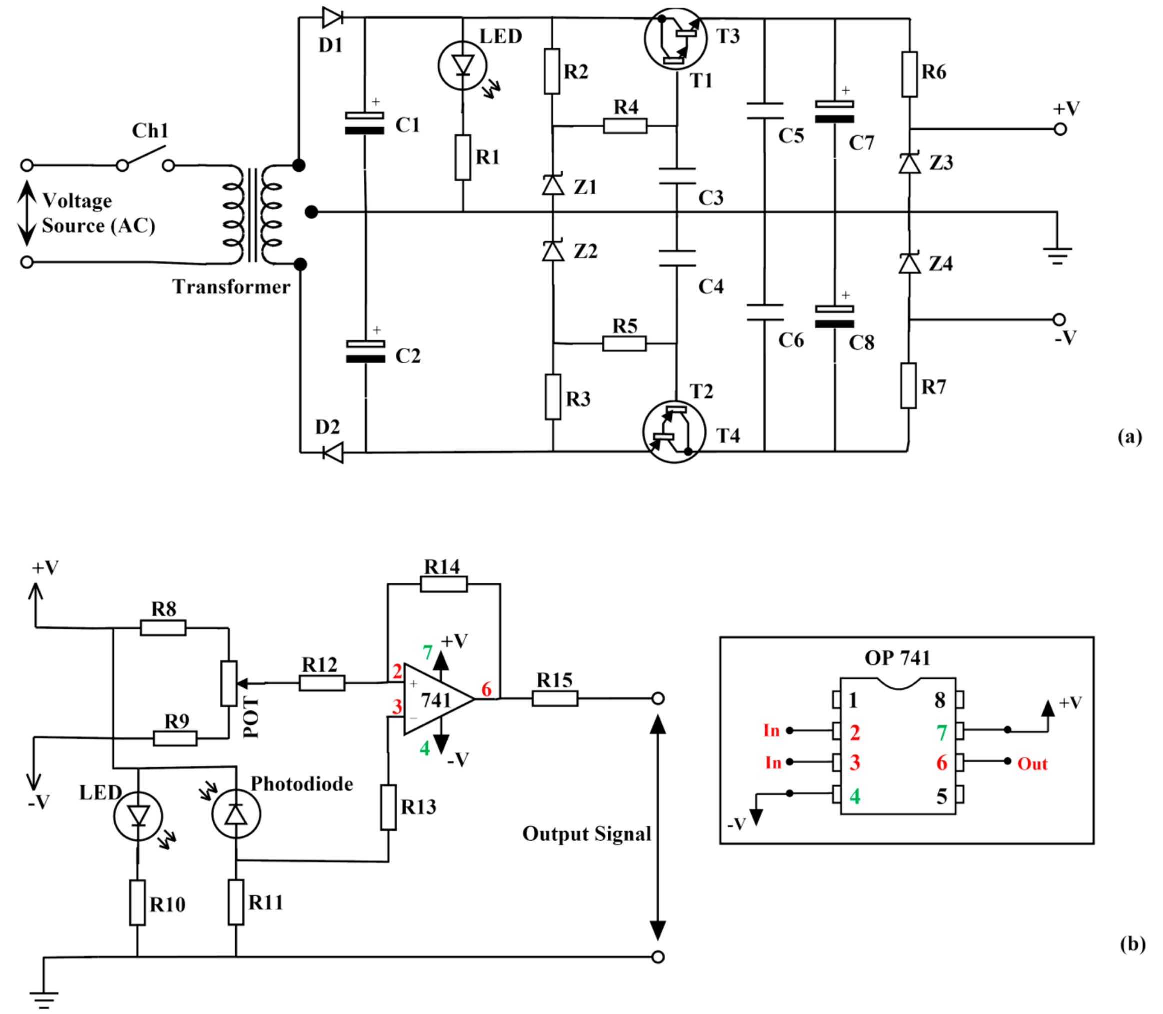

Figure 3. (a) Electrical circuit of the power source that supplies a 300 mA current output, with a voltage input of 110 V and output voltage of ±12 V. (b) Electrical circuit of the photometer. In detail, the OP 741 pin description.

Table 1. Detailed Description and Specification of Electronic Components in Figure 3

Circuit Components Specification[a]			
R6, R7, R10, R14	1 kΩ	C1, C2	2200 μF
R1, R2, R3, R4, R5, R15	2.2 kΩ	C3, C4, C7, C8	100 nF
R8, R9, R12	10 kΩ	C5, C6	100 μF
R11, R13	100 kΩ	Z1, Z2	1N4744/15 V
T1	BC548	Z3, Z4	1N4742/12 V
T2	BC558	Transformer	±15 V × 1.0 A
T3	TIP31C	POT	10 kΩ
T4	TIP32C	Integrated circuit	OP741

[a] R = resistor; C = capacitor; POT = potentiometer; Z = Zener diode.

solution input and other for solution output. A lid covers the cell and allows flow of the sample throughout. Figure 1b presents the photography of the cell and its holder.

Figure 2 represents the assembling of photometric titration system with the LED photometer as a detector, and optionally the potentiometric system, for comparison of the results.

Electronic Circuit of the LED-Based Photometer

The circuit was designed with a ±12 V power supply, a photodetection system composed by an LED light source and a photodiode used as a detector and an amplifier that sends the output signal to an external multimeter. Details of the power supply and the photometer circuits are presented below.

The power supply circuit, presented in Figure 3a, was built in order to prevent external fluctuations in the current providing a stable electrical feeding to the system that supplies a 300 mA current output, with an voltage input of 110 V and voltage output of ±12 V. The components present in Figure 3a are described in Table 1. The circuit is presented here, but there are many similar devices available in the electronics market. Thus, assembling the power supply is an Instructor's decision based on time and resources availability.

The input transformer presents a current range of up to 1 A, with a bivolt output of ±15 V. The rectifying diodes (1N4002) form a half-wave rectifying system. The output tension is filtered through the C1 and C2 capacitors (2200 μF), whose capacitance were calculated taking into account the filtering capacity required, the output current, the input voltage and the frequency source. The tension peaks dissipation is supported by TIP type transistors linked to aluminum heat dissipaters (2.5 cm × 3.0 cm × 0.2 cm, length, hight, and thickness, respectively). The filtering system is completed by R1, R2, R3, R4, and R5 resistors, coupled to the Z1 e Z2 Zener diodes (15 V), and the C5, C6, C7, and C8 capacitors. The Z3 and Z4 Zener diodes (12 V) fix the output voltage in ±12 V. T1 (BC548), T2(BC 558), T3 (TIP31C), and T4(TIP 32C) are also employed.

Figure 3b presents the electrical circuit of the photometer. Resistors R8, R9 and the potentiometer POT, regulate the output signal from the tension gain generated by the operational amplifier 741 and the R11 and R13 resistors. The LED acts as a light source, while the detection of the light from the glass cell is performed by the PHFT380 photodiode. In Figure 3b, there is an inset describing the connections of the integrated circuit OP 741. The complete list of components is presented in Table 1.

The PHFT 380 was chosen as a detector based on the fact that it presents a reasonable performance in the visible range for the emissions from the yellow, red, and green LEDs used in this work.

Alternatively, the final assembling can be performed using a printed circuit board and the flow-cell, both inserted in a plastic box. The complete circuit costs the equivalent to U.S. $50.00 in the Brazilian market, considering only the photometer and power supply circuits. Please refer to Supporting Information for a list of required materials.

Reactants and Solutions

The reagents were of analytical grade and used as received from Aldrich Chemical Co. All the solutions were prepared with water purified in a Barnstead (Easy pure RoDi) system.

Stock 0.10 mol L^{-1} NaOH, HCl and CH_3COOH (acetic acid, HAc) solutions were prepared. Sodium hydroxide was standardized using potassium hydrogen phthalate, and then used to standardize the HCl and HAc solutions, using a potentiometric procedure using a pH-meter (Corning 430) in the presence of a combined glass electrode (Metrohm EA-320).

Solutions of the following visual indicators were used with the LED photometer titrations: phenolphthalein, phenol red, bromocresol green, and bromothymol blue, all 1% (m/v).

Please refer to Supporting Information for more details on chemicals used.

Photometric Titrations

Titrations were performed with the basic titrant solution in a glass buret and the acidic solution in a beaker. A peristaltic pump (ISMATEC, IPC 4) was used to transfer the reaction mixture from the beaker to the flow cell, linked to the LED photometer. Alternatively, a glass electrode coupled to a pH-meter (Corning 430) and a combined glass electrode can be used to follow the pH changes during the procedure, for comparison. A magnetic stirrer was used to homogenize the solution, and 0.8 mm i.d. polyethylene tubing (Fiotubos, Brazil) was used to transfer the fluids. The assembly is schematically represented in Figure 1, in which a detail of the glass flow cell is also provided.

After each addition of the titrant, the mixture was homogenized. Then, the pump was turned on for 30 s in order to renew the solution in the entire circuit. Subsequently, the pumping was interrupted and the photometer output signal measured was with the help of a multimeter (Minipa, ET-2050), operating in the DC voltage mode. Alternatively, the pH and the solution color were simultaneously observed at each addition to detect the end point.

The color of the LED source was chosen accordingly to the indicator used in order to provide the highest change as possible in the photometer signal at the equivalence point. Please refer to Supporting Information for more details.

Finally, the changes in the electric potential difference as a function of the titrant volume added were plotted and used to determine the end point at the sudden signal change.

RESULTS AND DISCUSSION

The expected response of the photometer output signal is determined by a sudden change in the circuit output electric potential difference. It is provoked by the amount of light that reaches the photodiode, when the indicator changes its color at the equivalence point. Thus, two situations are possible. In the first case, the indicator absorbs the light from the LED before the equivalence point and does not absorb the light after the equivalence point due to the color change. So the response suddenly changes from a low electric potential difference output signal to a higher output in the multimeter operating in the voltage mode. The second possibility is the opposite, when the indicator does not absorb light before, but does so after the equivalence point. In this case, a sudden decrease in the signal is noticed.

Thus, the first step is the appropriate choice of the LED color, according to the system to be titrated and the indicator used. Table 2 resumes some features of the indicators used in this work that lead to the proper LED choice, which is based on the complementary colors concept.[15]

Table 2. Some Features of the Acid–Base Indicators Used and the Color LED Chosen

Indicator	pH transition range[a]	Color change[a]	LED choice
bromothymol blue	6.2–7.6	yellow - blue	yellow
bromocresol green	3.8–5.4	yellow - blue	yellow
phenol red	6.8–8.4	yellow - red	green
phenolphthalein	8.5–10.0	colorless - red	green

[a] Values obtained from ref 15.

To evaluate the performance of the LED photometer, a series of titrations was performed. The end points were determinated by electric potential difference vs volume of titrant graphs immediately at the volume in which the signal starts changing. Figure 4 presents the typical graphs obtained in the titrations of different acid–base systems: HCl (strong acid) with NaOH (strong base), HAc (weak acid) with NaOH (strong base), and HCl (strong acid) with NH_4OH (weak base).

The curves are just representative of the capabilities of the instrument and do not follow exactly the volume increments as suggested in the student's handout in Supporting Information.

In Figure 4a, the pH curve represents the titration of a strong acid with a strong base in which the pH increases slowly until near the equivalence point, where the pH suddenly increases with a small increase in the volume of base added. At the equivalence point, the concentration of acid $[H^+]$ is the same as that of base $[OH^-]$. After the equivalence point, in excess of base the pH slowly increases until the end of experiment. During the sudden pH increase, the phenolphthalein color

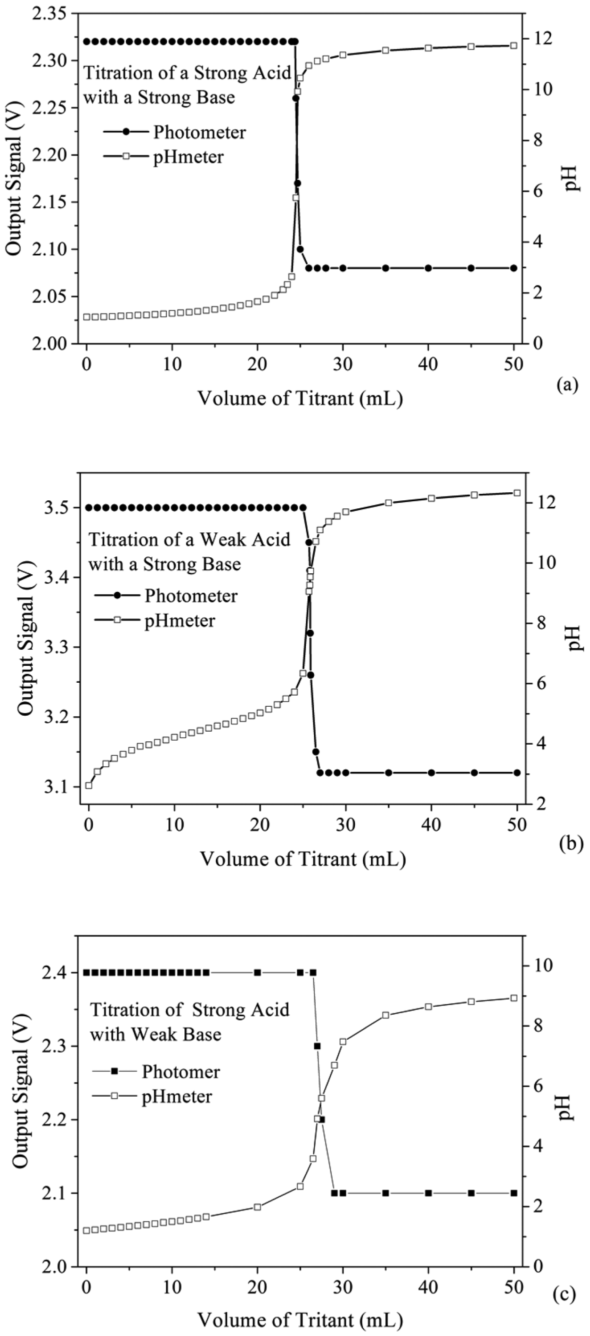

Figure 4. Photometric and potentiometric titration curves of (a) 25.00 mL of 0.091 mol L^{-1} HCl (strong acid) with 0.094 mol L^{-1} NaOH (strong base), with phenolphthalein as indicator; (b) 25.00 mL of 0.098 mol L^{-1} HAc (weak acid) with 0.094 mol L^{-1} NaOH, with phenolphthalein as indicator; (c) 25.00 mL of 0.106 mol L^{-1} HCl (strong acid) with 0.098 mol L^{-1} NH_4OH (weak base), with bromocresol green as indicator. Green and yellow LEDs were used for phenolphthalein and bromocresol green, respectively. Curves are representative of the instrumental capability and do not follow rigorously the volume increments suggested in students handout.

changes from colorless to red. Thus, the light from the green LED is absorbed by the indicator and the output signal from the photometer drops down once the photodetector receives lower intensity of light from the source.

For the titration of weak acid with strong base, Figure 4b, in the equivalence point, the pH is higher than 7 and can be observed by the photometric procedure using the phenolphthalein as acid/base indicator. Similar behavior for the photometric titration curve can be observed in this case, once the same LED was used as light source in the presence of the same indicator.

In Figure 4c, a strong acid is titrated with a weak base both at 0.1 mol L^{-1} level, resulting in an equivalence point at pH approximately 5. In this case, the indicator is the bromocresol green whose color changes from yellow into blue. With the use of the yellow LED, there is no light absorption before the equivalence point in acidic medium in which the indicator presents a yellow color. After the equivalence point, in basic medium, the indicator becomes blue and the light is now absorbed, resulting in a sudden decrease in the detector signal.

On top of this basic proposition, other features can be explored using the photometer, according to the instructor's planning and, of course, time availability, as described below. Of course, more time is required to perform these additional demonstrations than one 4 h lab.

To evaluate the effect of the indicator amount in the photometer response, titrations of 25.0 mL of 0.091 mol L^{-1} HCl with 0.094 mol L^{-1} NaOH are performed in the presence of different volumes of 1% phenolphthalein. The results are presented in Figure 5 using the phenolphthalein as indicator and the green LED as light source. Again, the curves are just representative of the capabilities of the instrument and do not follow exactly the volume increments as suggested in the student's handout in Supporting Information.

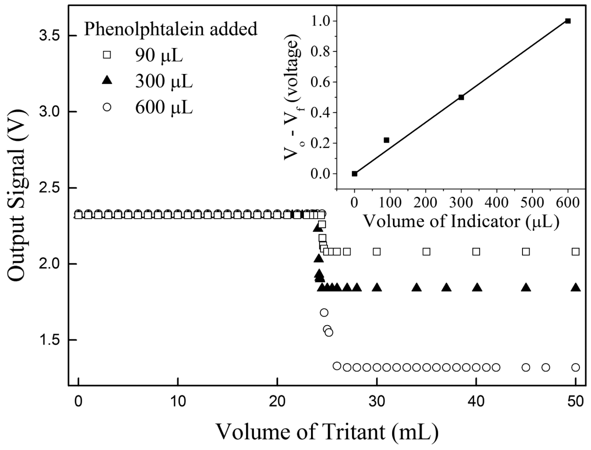

Figure 5. Titration curves of curves 25.0 mL of 0.091 mol L^{-1} HCl with 0.094 mol L^{-1} NaOH, in the presence of different amounts of 1% phenolphthalein, using the green LED as a light source. In the inset, ΔV ($V_0 - V_f$) vs indicator volume. The V_0 and V_f are the signal in the beginning and in the end point, respectively. Curves are representative of the instrumental capability and do not follow rigorously the volume increments suggested in students handout.

Although no changes are observed in the end point volume that remained at ca. 24.7 mL, as much indicator is present, deeper is the change in the output signal, in agreement with the Beer Law (inset in Figure 5). Thus, 1.00 mL of 1% phenolphthalein was chosen for further experiments.

Finally, the LED photometer was then used in the detection of the end point in the different acid−base titrations systems, that present different pH values in the end point in the presence of the different indicators presented in Table 2. The purpose of these studies was to determine the error caused by the different pH transition ranges in the end point of these

Table 3. Results from the Acid−Base Titrations Using the Photometer and the Glass Electrode in the Presence of Different LEDs and Indicators, as Well as the Calculated Ones

	V_{eq}/mL				
System (indicator)[a]	Photometric	Potenciometric	Calculated[b]	E_1[c]/%	E_2[d]/%
HCl−NaOH (pht)	24.7	24.5	24.2	0.8	2.0
HCl−NaOH (btb)	24.0	24.0	24.2	0	−0.8
HCl−NaOH (phr)	24.0	23.9	24.2	0.4	- 0.8
HCl−NaOH (bcg)	23.9	24.0	24.2	−0.4	−1.2
HAc−NaOH (pht)	25.9	25.9	26.1	0	- 0.8
HCl−NH_4OH (bcg)	27.2	27.0	27.1	0.7	0.4

[a] pht = phenolphthalein; btb = bromothymol blue; phr = phenol red; bcg = bromocresol green. [b] Considering: C_{NaOH} = 0.094 mol L^{-1}; C_{HCl} = 0.091 mol L^{-1}; C_{HAc} = 0.098 mol L^{-1}. [c] E_1 = [(photometric − potenciometric)/potenciometric] × 100. [d] E_2 = [(photometric − calculated)/calculated] × 100.

titrations, when compared with the potentiometric and calculated values. The different color changes were detected using an LED chosen according to the complementary colors in Table 2.

Table 3 presents the results of titrations in comparison with those obtained by potentiometry with the glass electrode using these systems, and using all indicators for the HCl−NaOH system. The small differences in the errors for the photometric detection in relation to those for calculated equivalence volumes and those from the potentiometric methods were attributed to the experimental errors as those in volume transfer and others systematic errors.

The resulting curves for HCl−NaOH titrations in the presence of the different indicators are presented in Figure 6. In this figure, a dashed line presents the potentiometric average equivalence point, and is clear that the bromothymol blue and phenol red, whose transition pH range are close to 7.0, are the best choices of indicators. Again, the curves are just representative of the capabilities of the instrument and do not follow exactly the volume increments as suggested in the student's handout in Supporting Information.

As predicted by the theory[15,16] and demonstrated here by LED photometer procedure in Figure 6 and data in Table 3, the bromothymol blue is more accurate for strong acid/strong base system, in which the end point pH is 7.0, while phenolphthalein is more recommended for the weak acid/strong base system, which presents an end point at pH > 8, depending on the concentrations of the reactants.

HARZARDS

- Potassium hydrogen phtalate may cause eyes irritation.
- Hydrochloric acid causes severe skin burns and eye damage, and may cause respiratory irritation.
- NaOH solid is corrosive and causes severe skin burns and eye damage. The NaOH solution is corrosive and should be handled with care.
- The indicators: phenolphthalein, bromocresol green, phenol red and bromothymol blue in high concentration can become toxic upon ingestion.

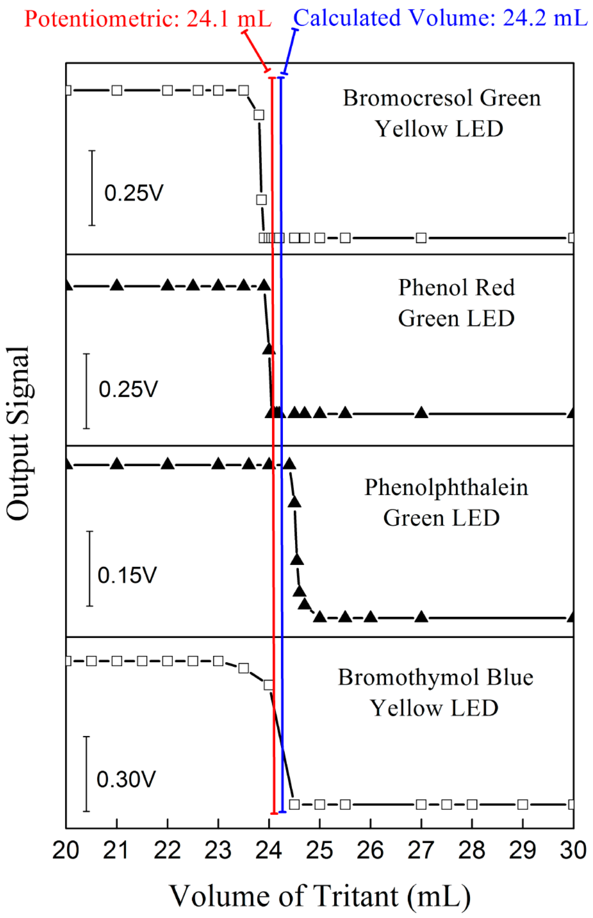

Figure 6. Titration curves of 25.00 mL of 0.091 mol L^{-1} HCl with 0.094 mol L^{-1} NaOH, in the presence of different indicators and using the appropriate LED as a light source. Dash line expresses the potentiometric average value, and the dot line expresses the calculated average value. Curves are representative of the instrumental capability and do not follow rigorously the volume increments suggested in students handout.

FINAL REMARKS

This article describes a laboratory experiment suitable for use in undergraduate analytical chemistry courses: a low-cost photometric apparatus based on LED component as the light source to be applied in acid−base titration. The simple electronic requirements are essential to use the homemade photometric circuit in the development of inexpensive instrumentation for the undergraduate analytical chemical laboratory, which permitted demonstrating several fundamental principals in acid−base chemistry, basic spectrophotometry and photometric titrations.

If the instructor has all the material in hands, including the circuit board and electronic components, the flow cell and its support, in a class we spent 1 to 2 h to introduce the system and assembly the circuit. Of course the instrumental assembling will depend on the time availability.

In a practical evaluation with students working in groups of three members, each titration took ca. 60 min to be completed. Thus, the introduction, instrument assembly, and acid–base titrations presented in Figure 4 can be performed in a 4 h class. If the instructor decides to demonstrate the effect of indicator amount and the error provoked by different indicators choice, of course more time will be required.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Description of the material and equipment. Notes for students and instructors, photometer construction, chemical standardization, experiment procedures and data handling. This material is available via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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