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Optical Sensors for Manual and Automatic Titration in Undergraduate Laboratory

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ABSTRACT The classic undergraduate titration analysis is upgraded using instrumental detection of end point with color indicators. Several color sensors (CCD-based spectrophotometer, video camera with RGB digitalization, photodiode with appropriate filters) were tested in order to replace the visual indication of the end point with different indicators. The developed procedures show adequate characteristics such as a short titration time and accuracy of 0.1–1%. Specific features of particular titrations such as hardness of water and argentometric titration of chloride are discussed. In the author's opinion, this experimental setup represents an affordable (\$100-level) option for an undergraduate or advanced high school chemistry laboratory.

KEYWORDS CCD spectrophotometer, indicator, optical sensor, photodiode, titration

INTRODUCTION

Titration experiments take up a great part of the contemporary general chemistry and analytical chemistry laboratory.^[1,2] Some titrations employ electrodes for the determination of the end point; argentometric titrations with Ag electrode, acid-base titrations with pH electrode, and Karl Fischer titrations with voltammetric indication are among the most common. Historically many procedures utilize visual indication of the end point: various pH indicators in acid-base titration, metal indicators for titrations with EDTA and precipitation titrations, and starch in iodometric titration are often used in the undergraduate laboratory.

It is an attractive option to substitute visual indication of the end point with the instrumental spectrophotometric device. There are two separate reasons for using a spectrophotometric sensor. First and most important, it makes possible running an automatic titration as easily as with electrochemical sensors.^[3] Another often-overlooked factor is the color blindness of a significant fraction of population (and, of course, of many students). Colorblind people can recognize a wide range of colors yet find it difficult to distinguish certain colors. The frequency of colorblindness is fairly high; around 5% of males are so-called “red-green” colorblind.^[4] Optical sensors remove the color blindness problem; they also can be used in UV and NIR ranges where all of us are blind.

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Commercial systems for photometric titration were first developed in 1950; various early designs are described in detail.^[5] Two main designs were suggested: (a) internal titrations, with measurements performed directly in a titration vessel; and (b) external titrations, where samples are taken from the titration vessel; for automatic titration, in this design the solution is circulated through the flow cell.^[5–7] With optical fibers' becoming available, various immersion optical sensors were successfully employed.^[8–13] The use of color video camera as an optical sensor was described.^[14] For research instruments, the necessity of high precision is often emphasized.^[6] Despite the success of internal titration instruments, the convenience of the external measurement by high-precision instrument still makes it an attractive alternative.^[15]

Most of internal systems have a disadvantage that prevents them from use in the college laboratory: a very high price. For example, an additional optical fiber adds several hundred dollars to the cost of titration setup. Low-cost alternatives suitable for college were developed. The setup^[16] uses an LED as a light source with a specific wavelength and a phototransistor positioned from the opposite side of the titration vessel. Because no computer is employed, an appropriate circuit needs to be assembled by students or by the teacher.

In this paper, I test three different types of commercially available photometric devices in order to find an affordable option for an undergraduate laboratory with 12–18 students. It is assumed that the laboratory already has a necessary number of computers equipped with serial and USB connections. Some of these devices as well as CCD spectrophotometers can also be used in other educational experiments including qualitative spectral analysis of metal ions.^[17,18]

Traditional photometric titration often requires high precision of photometric measurements with three or even four significant digits. This is unnecessary when performing common titrations with visual indicators. Even with a relative error in absorbance of around 10%, one can estimate the end point of titration with the precision of three or even four significant digits. The explanation is straightforward: taking into account high molar absorptivities of most color indicators, the change of 0.1 absorbance units requires a change in concentration of the colored

form of the indicator by less than 10^{-5} mol/L. With the concentration of analyte being around 10^{-2} mol/L, the indicator error is around 0.1% and can be made even smaller if necessary by titration of a blank solution. Therefore, the absorbance measurements we need require two-digit (6–7 bit) numbers only. Spectral requirements are also very relaxed: the visual indicators have absorption bands at least 30–50 nm in width and do not require high resolution. This should not be surprising since visual indicators were selected with the very low spectral resolution of the human eye in mind.

MATERIALS AND METHODS

General

In this work, a 10-mL class A glass burette was used for manual measurements and a home-made automatic titrator connected to a PC via serial port was employed for automatic and semi-automatic titrations. For automatic titration, the titration rate was constant during the whole experiment at around 1 mL/min; the precision of burette was about 0.01 mL. A 100-mL beaker was placed on a small magnetic stirrer; the stirring rate was adjusted to achieve a relatively small and stable vortex at the surface. The sensor was positioned next to the beaker just above the stirring bar (and, importantly, below the vortex).

Sensors Tested

CCD Spectrophotometer

A multiwavelength CCD spectrophotometer with an immersion probe is almost ideal titration sensor. A beam from a strong light source shines through the optic fiber into a partly open chamber/cell, is reflected by a mirror, and travels back by another optic fiber to the spectrophotometer unit. Such probes and appropriate light sources are commercially available. Unfortunately, the total cost of such system would be at least \$2000 in addition to the cost of the spectrophotometer, which is above the level of an undergraduate laboratory.

When the exact values of absorbance are not sought, this setup can be significantly simplified by using incandescent lamp as a light source and placing a spectrophotometer next to the titration

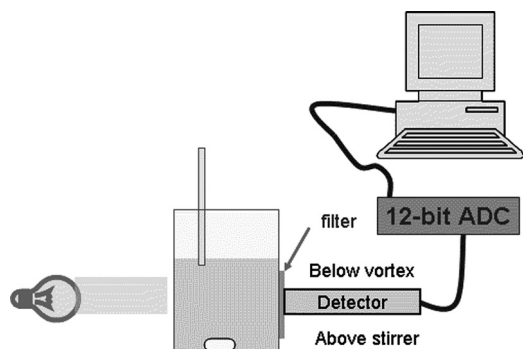


FIGURE 1 Scheme of sensor position.

beaker. The quality of measurements is sufficient for correctly establishing the end point of titration.

Light Intensity Sensor Based on Si Photodiode

A Hamamatsu S1133 Si photodiode with sensitivity ranging from 320 to 730 nm and peak response at 560 nm was connected to a PC via a 12-bit ADC of Vernier LabPro (Vernier Software & Technology, Beaverton, OR) interface.^[19] An additional filter was placed in front of the sensor to reduce the bandwidth of incoming light. See Fig. 1.

USB Video Camera

With a low-end USB video camera we essentially have an 8-bit photometer with three channels: red (600–620 nm), green (540–550 nm), and blue (460–480 nm). The appropriate software is available to collect the corresponding RGB values manually while observing the video image on the screen (ColorPic v.4.1, iconico.com) or to automatically plot RGB values as a function of time (RoboRealm V.2.5, Iconico, New York, NY) and relate them to the automatic burette data. The definite advantage of the camera is its widespread availability. When using the camera as a titration detector, it is important to suppress the automatic adjustment of gain and color correction and to have a white background behind the titration vessel.

RESULTS AND DISCUSSION

With relatively high concentrations of titrant (0.05–0.2 M), the color of the indicator changes almost instantly, resulting in a sharp change of sensor reading. For example, when HCl solution is titrated with NaOH using methyl red as indicator, the absorbance

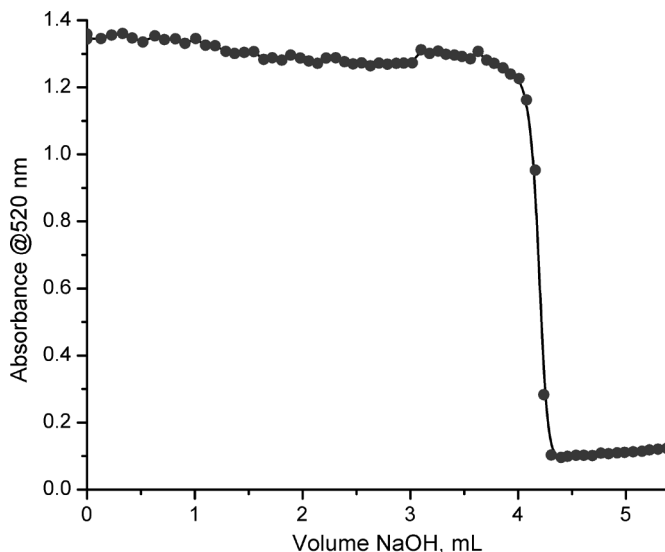


FIGURE 2 Automatic spectrophotometric titration of hydrochloric acid with sodium hydroxide using methyl red indicator.

of the solution at 520 nm decreases by one absorbance unit within 0.05-mL range of titrant volume (Fig. 2). The corresponding change of RGB values was from 145, 7, 20 (“Red”) to 130, 130, 20 (“Yellow”). With error of absorbance readings not higher than 0.1 absorbance units or readings of G component of around 10 units, it is feasible to find the end point with the same accuracy as with the burette (around 0.01 mL in our case). The similar sharp changes were observed for iodometric titration with starch as indicator. It needs to be mentioned that in these cases the visual detection of end point is straightforward, and photometric titration is advantageous only in an automatic mode. See Fig. 2.

Hardness of Water

Determination of the hardness of water is one of the most common laboratory assignments in AP chemistry class and in the university general chemistry laboratory. It often uses low concentration of titrant and is more challenging.^[1–3,20] The following procedure was employed for this titration:

To a 50-mL aliquot of the solution, 3–5 mL of ammonia buffer (pH 10) is added. Two or three drops of 0.5% eriochrom T indicator solution are sufficient to make the solution intensely colored. In visual titration, the resulting solution is titrated with EDTA until the red-pinkish color changes into clear blue. Color change is very sharp for large concentrations of magnesium ions. Some natural water

samples contain calcium along with magnesium along with small quantities of transition metal ions. These ions form very stable colored compounds with the indicator; these compounds are not titrated with EDTA and do not change color (indicator is “blocked”). It is difficult or even impossible to detect the ending point visually without masking the interfering ions with cyanide ion.

All three sensors demonstrate good performance in titration of magnesium ions (Figs. 3 and 4). The increase of absorbance at around 600 nm ($\lambda_{\text{max}} = 615 \text{ nm}$, free indicator) is simultaneous with the decrease of absorbance at 530 nm (complex compound with magnesium ion). A red filter that cuts off light with $\lambda < 600 \text{ nm}$ performs in a way very similar to that of Red in video camera.

In an ideal curve, the end point is the intersection of two straight lines. Some roundness in the vicinity

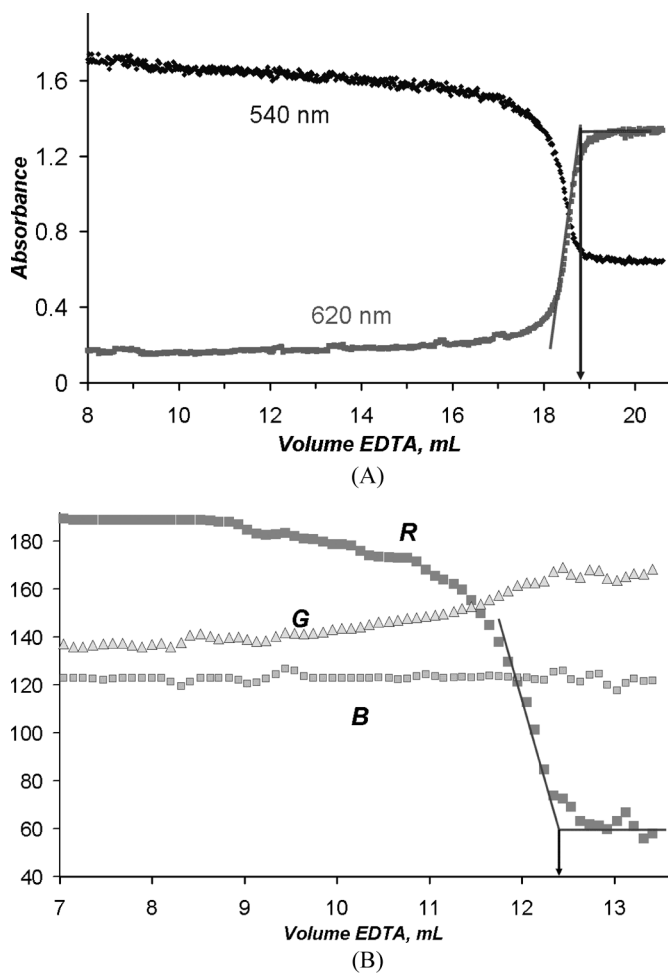


FIGURE 3 Automatic titration of magnesium ions with 0.00500-M EDTA using (A) OceanOptics Red Tide spectrophotometer as a detector and (B) RGB values from the Logitech web camera.

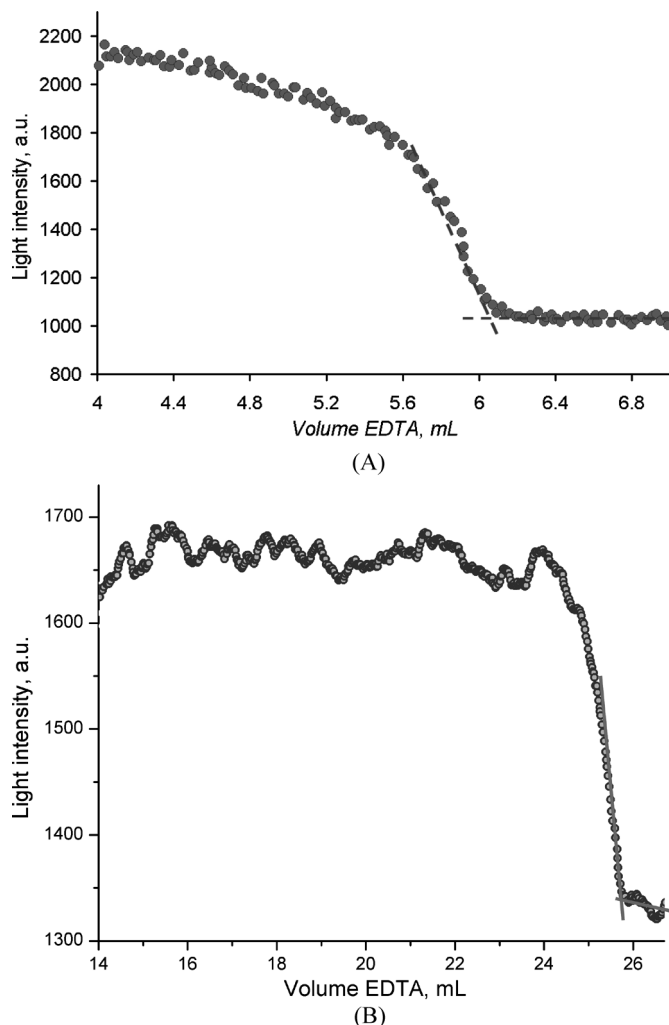


FIGURE 4 Automatic titration of (A) magnesium ions and (B) contaminated water sample with 0.00500-M EDTA using Hamamatsu S1133 photodiode with red filter. The decrease in light intensity is much smaller for contaminated water.

of the end point appears due to (a) delay because of inadequate stirring and (b) some dissociation of metal–indicator complex in solution. Titration plot consists of two straight lines extrapolated to intersect at end point. To simplify the decision-making in automatic titration, the end point of titration is sometimes^[3] artificially positioned at the steep portion of the titration curve resulting in some under-titration. The error does not exceed 0.01–0.02-mg Mg, which is practical for a 50-mL sample.

When a high concentration of interfering ions is present (Fig. 4B), the visual detection of the end point is practically impossible. Nevertheless, the end point is relatively easy to detect using the red-filtered sensor. Despite the dramatic decrease in the color jump, it is still sharp enough for

unambiguous end point detection. It allows the titration of any natural samples without using toxic potassium cyanide^[20] as a masking agent.

Precipitation Titrations

Opaque solutions, which are common in precipitation procedures, present an additional challenge to photometric measurement. In this case, the intensity of the transmitted light depends not only on absorbance by the indicator but mostly on scattering. Nevertheless, a reflection-based approach using the video camera gives sufficient results. Here we show the results of argentometric titration of chloride ion (Fig. 5).

Chromate-ion (Mohr titration) and dichlorofluorescein (Fajans titration) were used as color indicators. The color of a turbid solution changes from yellow to red or pink with simultaneous change of

turbidity because of the coagulation of AgCl colloid precipitate. In Mohr titration, the color does not change before the end point. In both cases, yellow or yellow-orange opaque solutions with R and G numbers being very close to their maximum value of 255, and with B being somewhere around 200 quickly change numbers for Blue and Green at the end point.

In practice, the use of Ag electrodes might be preferential to the visual indicator titration; the introduction of video camera (certainly less expensive than pH/mV meter with a set of electrodes) makes the indicator approach competitive.

CONCLUSIONS

The main obstacle to receiving high-quality results is the instability of the incoming light due to stirring; this need to be reduced to the level not exceeding 10% of total light intensity. The high spectral resolution offered by a CCD spectrophotometer does not give an advantage in any titration that I have tested. Nevertheless, the cheaper CCD spectrophotometers with resolution of around 10–20 nm might be better as titration sensors. Another possible option can be a color sensor based on a set of photodiodes with three or four preinstalled filters. A variable speed burette that will slow the titration rate in a vicinity of the end point would be another helpful improvement. All these options employ standard blocks that can be assembled in several minutes next to computer, which uses freeware or software that is already available in most educational institutions (for example, MS Excel). Therefore it is feasible to assemble six to eight titration stations in the laboratory that is used to teach titration procedures.

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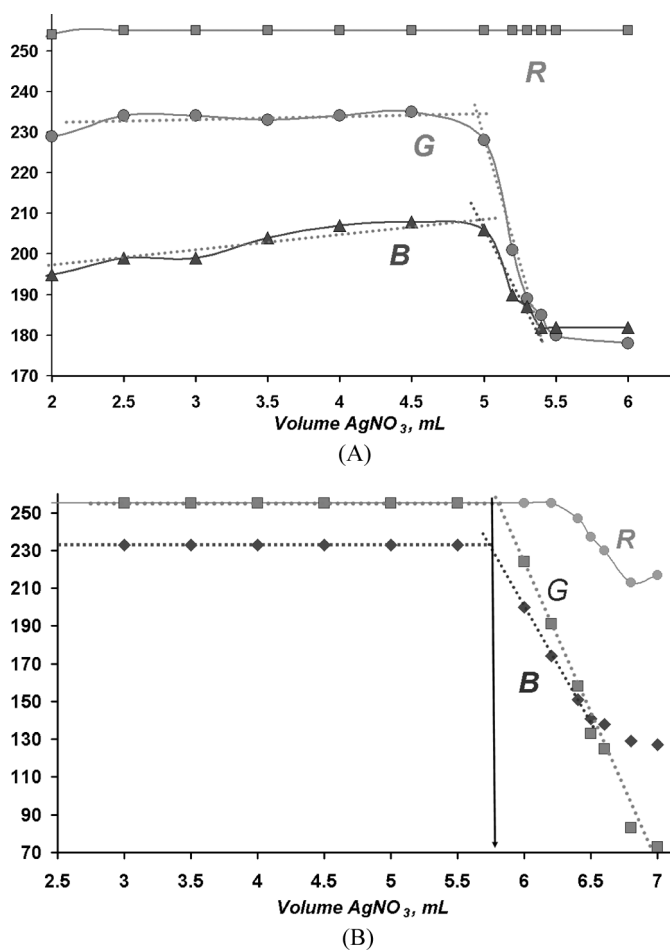


FIGURE 5 Manual argentometric titration of chloride with dichlorofluorescein indicator (Fajans method; (A) and with chromate indicator (Mohr method; (B) using RGB values.

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