
Computer Vision in Chemistry: Automatic Titration

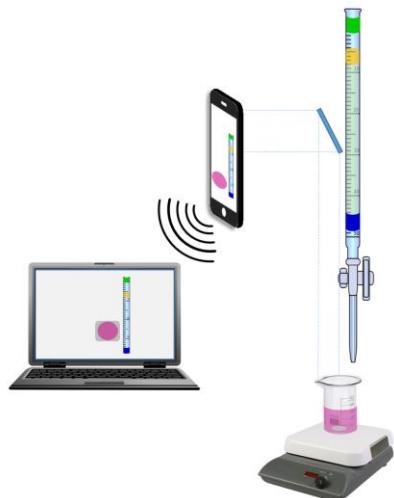
Yana Kosenkov, and Dmitri Kosenkov*

Department of Chemistry and Physics, Monmouth University, 400 Cedar Avenue, West Long Branch, NJ 07764

5 **ABSTRACT**

A novel technology that employs computer vision (CV) to carry out an automatic titration experiment is presented. The experiment is designed to facilitate understanding the basics of the CV technology and its application in chemistry among undergraduate students. The standard chemical procedure of titration has been chosen, since it is well known to students who completed general chemistry or similar foundation chemistry courses. A significant advantage of CV-based automation is the use of open-source software and readily available electronic devices, as no expensive specialized equipment or proprietary software is required. The experiment can be performed remotely, either live online or with pre-recorded videos. The reported technology is accessible to virtually any educational institution as well as to individuals. The proposed technology provides affordable and safe means for remote execution of titration experiments for students with disabilities. Therefore, the proposed experiment is suitable for traditional laboratory instruction, as well as remote synchronous or asynchronous course delivery which gained practical importance during the COVID-19 pandemic. Finally, the proposed CV-based automation opens a new realm of opportunities for rethinking traditional chemistry procedures where computer vision is used to improve performance of standard laboratory instruments and techniques.

ABSTRACT GRAPHIC



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KEYWORDS

First-Year Undergraduate / General, Upper-Division Undergraduate, Analytical Chemistry, Physical Chemistry, Laboratory Instruction, Internet / Web-Based Learning, Laboratory Equipment / Apparatus, Laboratory Computing / Interfacing, Titration / Volumetric Analysis.

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INTRODUCTION

Robotic laboratory platforms are capable of performing complex tasks such as automated chemical experiments.¹⁻³ Recent publications in this Journal have demonstrated a variety of ways to implement such modern technologies into undergraduate chemistry curricula, for example, custom experiment automation with microcontrollers (Arduino or Raspberry Pi)⁴⁻⁹ and 3D printing.⁹⁻¹² Performance of many intelligent devices (automatic instruments and robots) requires acquisition and processing of complex visual sensory input. Such processing commonly employs certain elements of artificial intelligence and widely relies on machine learning methods.¹⁻³ Computer vision (CV) is a technology suitable for acquisition, processing, and analysis of visual inputs (e.g., digital images), and, therefore, is an important integral aspect of modern laboratory automation. The present report focuses on implementing CV technology into the undergraduate chemistry laboratory curriculum. Development of modern undergraduate chemistry laboratory courses (e.g., general chemistry, quantitative analysis, physical chemistry, etc.) is challenging for multiple reasons. For instance, while these laboratory courses must cover fundamental chemistry topics, there is a clear preference among students for learning using novel, rapidly-developing technologies that may be used in academic research, clinical laboratories or industrial

50 settings (e.g., robotics and automation). The laboratory unit reported here introduces computer vision in the context of a titration experiment. Titration is a standard laboratory technique of quantitative chemical analysis that is well known to chemistry students and instructors. Here we propose a novel modification of the titrator that does not require any specialized hardware beyond what would be used for a standard laboratory titration with
55 phenolphthalein indicator. Only a web camera or smartphone is needed to take advantage of CV technology. Thus, the unit provides both reinforcement of fundamental concepts on acid-base reactions and a demonstration of modern era laboratory automation.

As development of novel laboratory instruments often requires appropriate software, the widespread use of *Python* and *JavaScript* programming languages, as well as several
60 other proprietary platforms,^{4,6-7} provides instructors with a toolkit to design and carry out chemistry experiments in teaching laboratories. A particular challenge is that, unfortunately, chemistry majors are not commonly exposed to advanced (and sometimes even basic) topics in computer programming and this hinders their efficient usage of computer technologies mentioned above. Thus, this report along with previous
65 publications in this Journal¹⁴⁻⁹ aims to fill this gap at least partially and provide a foundation for instructors to cover these topics in undergraduate labs. The described technology is based on free, open-source *Python* code. The titration experiment can be performed in a laboratory setting where a webcam/smartphone is used to monitor the experiment, as well as remotely - either live or with pre-recorded videos (e.g. YouTube¹³)
70 that are analyzed with provided software. The completely remote mode of operation of the proposed technology makes it a useful tool for online or hybrid instruction that is currently in high demand due to the Covid-19 pandemic.¹⁴⁻¹⁶ The proposed report consists of a description of CV technology basics followed by the automatic titration experiment. This technology helps students to learn basic elements of computer vision
75 and apply the technology to carry out the automatic titration experiment.

MATERIALS

The proposed technology requires standard equipment and materials needed to carry out a straightforward titration experiment with phenolphthalein indicator as described
80 elsewhere.¹⁷ Additionally, a computer with a webcam or a smartphone is required to capture a video stream. The required free software packages are listed in supporting materials (see S1). A summary of equipment and materials needed to carry out the experiment is as follows.

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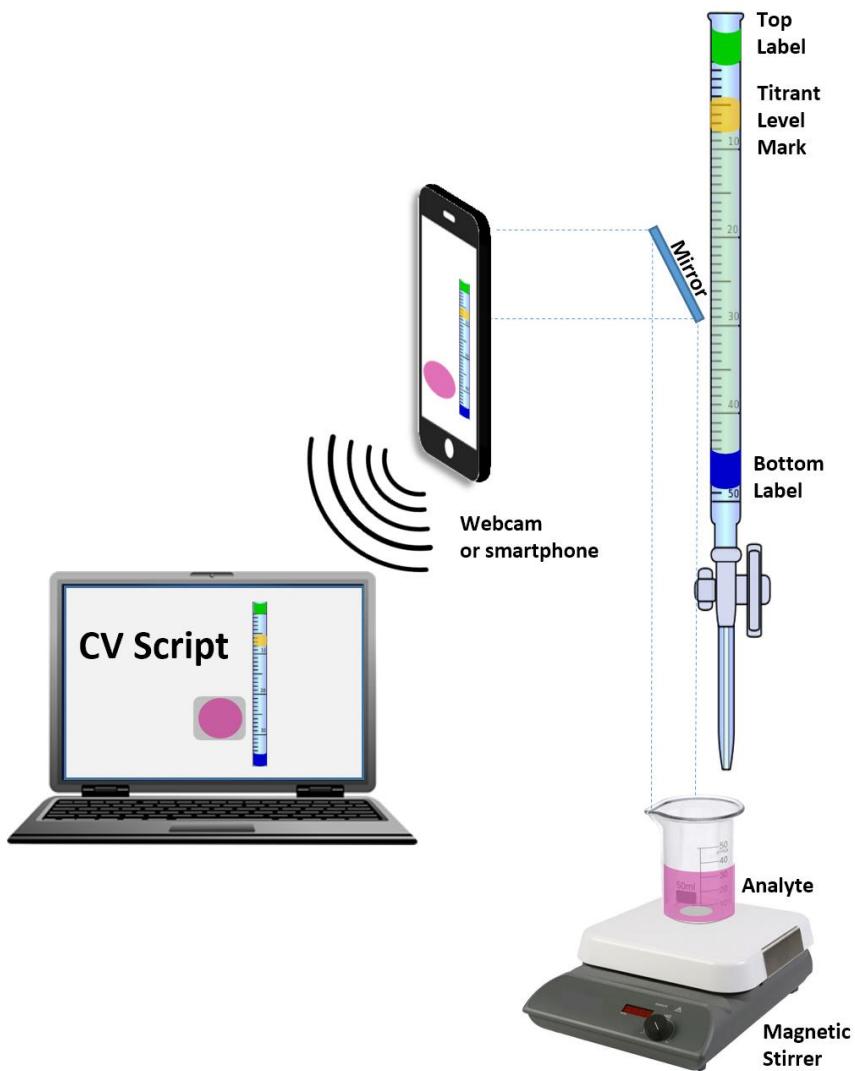
1. Phenolphthalein pH Indicator 1% Solution
2. Sodium hydroxide standard solution, 0.1M (Fisher scientific)
3. Hydrochloric acid standard solution, 0.1M (Fisher scientific)
4. Magnetic stirrer and stirring rod

5. Burette with stand
90 6. 3-prong clamp
7. Beaker, 20 mL
8. Graduated cylinder, 10 mL
9. Multicolor plastic (polyethylene) beads
10. Mirror ~50x50 mm²
95 11. Two-sided tape for mirror mounting
12. Multicolor labeling tape
13. Web camera or smartphone with stand
14. Desktop or laptop computer

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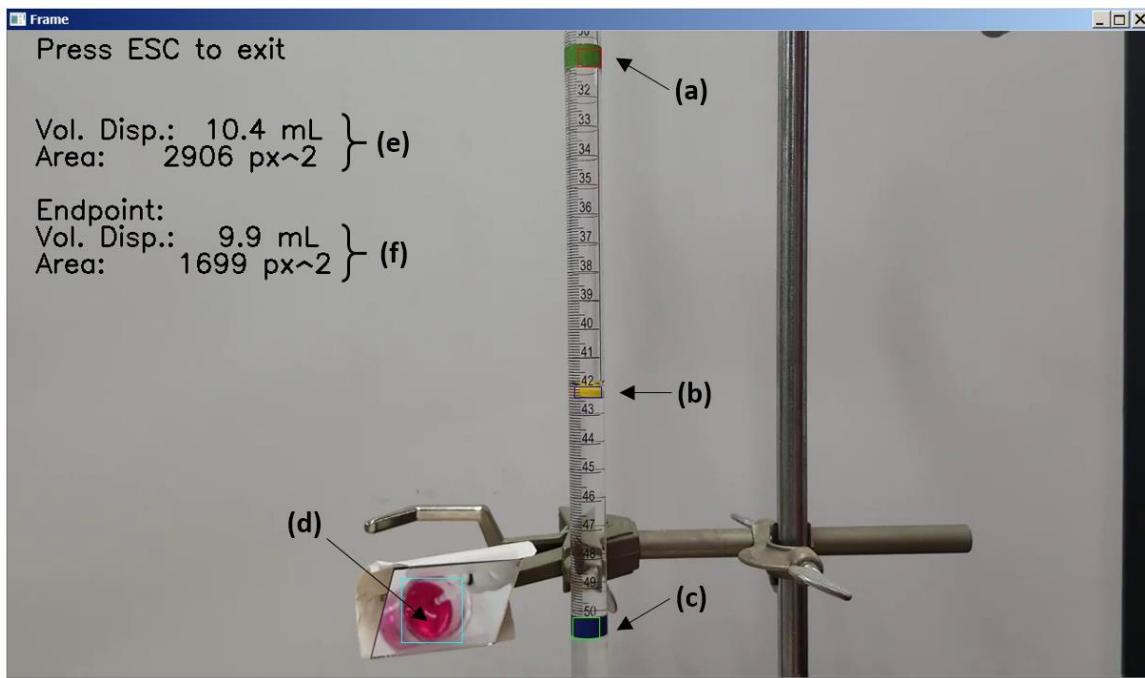
EXPERIMENTAL SETUP

The experimental setup is shown in Figure 1. First, a standard setup for a titration with an indicator is constructed as described elsewhere.¹⁷ The following modifications to the experimental setup are then made to carry out the proposed automated experiment:
105 a webcam or a smartphone is installed in front of the burette. A mirror is mounted on the burette stand to reflect a top-view of the beaker with the analyte solution to the webcam/smartphone. A standard laboratory 3-prong clamp and two-sided tape are used to mount the mirror. A free-floating plastics bead (e.g. polyethylene) is placed inside the burette to mark the level of titrant. Position of the free-floating bead marks the level of
110 the titrant in the burette. In this experiment the titrant is free dripping so that each drop dispenses approximately 0.1 mL of the solution (the rate can be manually adjusted if needed). The burette is labeled with two colored labels to indicate minimal (top label) and maximal (bottom label) volumes of dispensed titrant. The colors of the labels must be different from each other, from the color of the free-floating bead, and from the color of
115 the analyte solution. In the proposed experiment the following colors were chosen: top label – green, free floating bead – yellow, and bottom label – blue. Selection of easily distinguishable colors is essential for proper operation of the CV script. Sample label colors and color codes are provided in the supporting materials (see S2). A screenshot of the CV script is shown in Figure 2. It is noteworthy that the standard ambient lighting of
120 office and laboratory spaces (200-500 lux)¹⁸ is sufficient for reliable performance of the CV script after calibration (see below).



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Figure 1. Experimental setup: a standard burette is labeled with top and bottom label marks to indicate minimal and maximal volume of the titrant. A free-floating bead is used to indicate the level of titrant. A top-view image of the analyte solution is projected to the webcam/smartphone by the mirror. The CV script installed on the computer performs automatic analysis of the titration experiment progress.



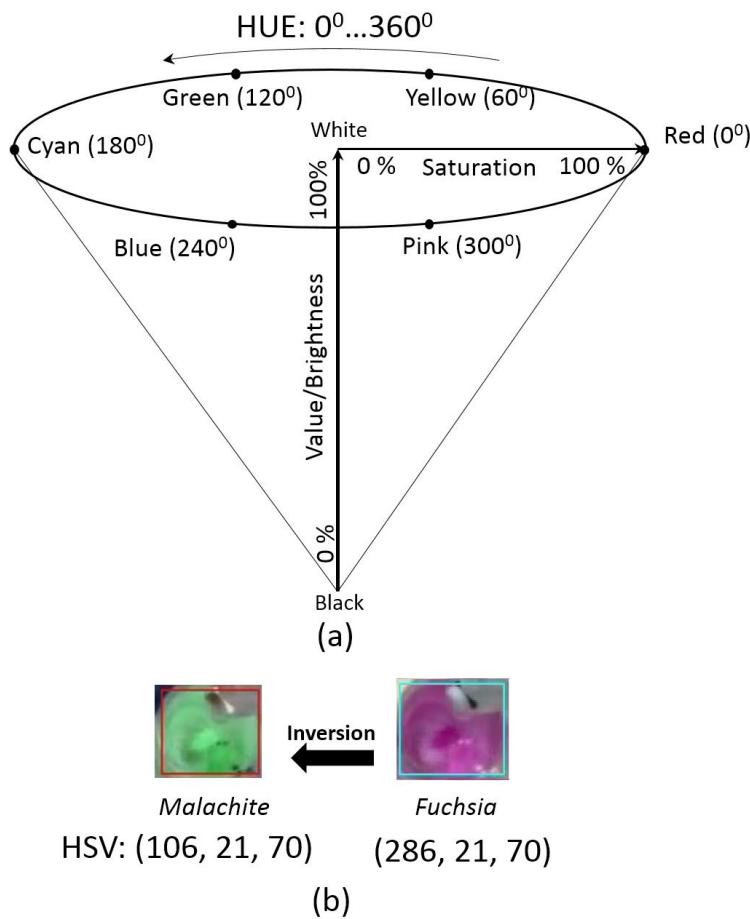
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Figure 2. Screenshot of the CV script window: (a) top mark; (b) titrant level mark; (c) bottom mark; (d) mirror image of the analyte solution; (e) interactive and (f) endpoint of titration data on volume of the dispensed titrant solution and area of the fuchsia (pink) spot. The script automatically tracks marks and the fuchsia spot outlining them with rectangles. The video recording is available at: <https://youtu.be/QBwOgb6VbU&t=4m16s>

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Calibration and Automatic Titration Procedure

The calibration and automatic titration are performed with the open-source *Python*¹⁹ script that utilizes *OpenCV* computer vision library.²⁰ A complete source code of the script and detailed experimental procedure are provided in supporting materials (see S3-S6). In 140 short, the script initially runs in the *calibration mode* that produces a photographic image of the burette with top, floating titrant level, and bottom marks. Also, solution of NaOH with phenolphthalein is used for calibration to define color at the endpoint of titration. The image is analyzed manually in the graphic editor (e.g., GIMP²¹ or Photoshop²²) to determine color codes of labels and the analyte solution for initial calibration of the script.



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Figure 3. (a) HSV color space used in the CV script; (b) Fuchsia color of the analyte solution is inverted to obtain malachite color which hues are easier to recognize by the CV script.

In the proposed experiment an HSV (Hue Saturation Value)²³⁻²⁴ color space is used to encode colors of the labels and analyte solution. It is common in CV processing to use the 150 HSV model instead of RGB (Red Green Blue) color for convenience of adjustment of brightness and color saturation. This is important for recognition of physical objects, since their colors are non-uniform and contain multiple shades of colors depending on the shape and position of the object with respect to the source of light. For example, a color of the 155 analyte solution at the endpoint of titration with phenolphthalein is fuchsia (pink) (Figure 3). From analysis of the calibration image in a graphic editor, (Figure 3) the color has the following code in the HSV color space: (286, 21, 70) where the hue is 286, saturation is 21%, and brightness (value) 70 %. However, for proper recognition of the endpoint of 160 titration a wider range of colors has to be included with saturation values from 21% to 98% and brightness from 70% to 100%. Another difficulty in recognition of fuchsia color is due to its similarity to red color which has hue: 0° on "the color wheel" and two numerical ranges are needed to cover fuchsia color and its hues: e.g. 0° ...2° and 286°...360°. In order to avoid the need of having two ranges for recognition of fuchsia

colored solution, the color of the image is first inverted, which effectively replaces red color (hue 0°) with cyan (hue 180°) and converts fuchsia to hues of malachite color. Finally, after 165 inversion of the image, the following range of colors is used to reliably determine the color corresponding to the endpoint of titration: (106, 21, 70) -(182, 98, 100). Similarly, color codes for top, floating, and bottom markers (although without color inversion) are recognized by the CV script. Color codes for all labels are provided in the supporting materials (S.3). This color information along with the information about colors of all marks 170 is supplied to the CV script. Once the script recognizes the marks on the burette and the free-floating mark, the volume of the titrant in the burette is automatically determined. Coordinates of the burette and free-floating marks are used to determine coordinates of 2D vectors: \overrightarrow{AM} and \overrightarrow{AB} in the plane of the image (Figure 4). The volume of the titrant V is determined with the following equation:

$$175 \quad V = V_{AB} \frac{|\overrightarrow{AM}|}{|\overrightarrow{AB}|} \quad (\text{Eq. 1})$$

where V_{AB} is the maximal volume of the titrant between upper and lower marks on the burette. This approach for determination of volume also enables correct calculation of volume even if the camera is tilted and the burette is not perfectly vertical on the image (i.e., the “horizon line” of the image is not perfectly leveled). Initially the maximal volume 180 and initial volume of the titrant is supplied to the CV script then the script automatically tracks the volume of the dispensed titrant and prints the dispensed volume on the screen (Figure 2).

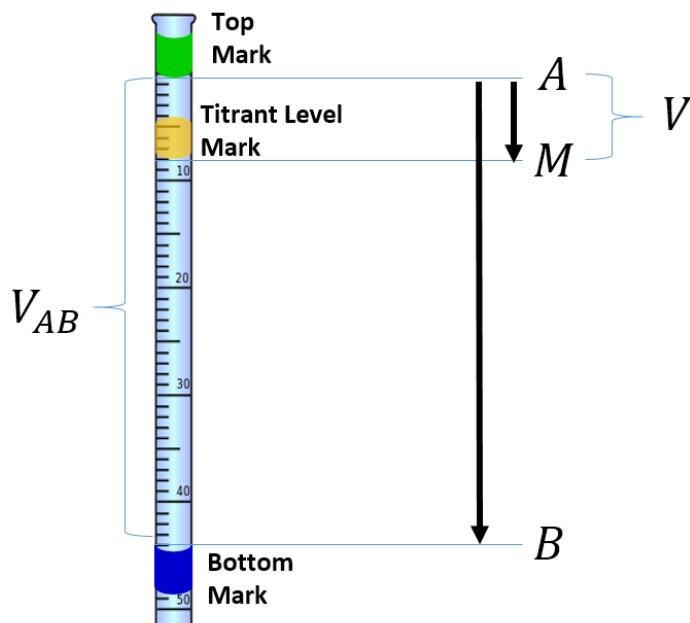
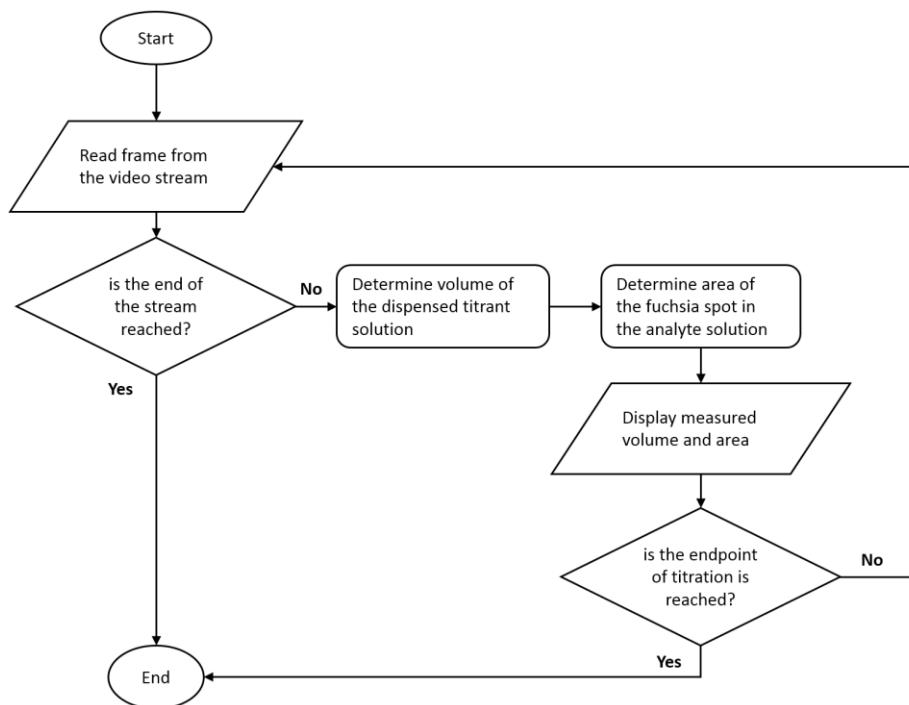


Figure 4. The volume of the titrant solution is determined based on coordinates of vectors \overrightarrow{AB} and \overrightarrow{AM} (see explanation in the text)

185 Next, the CV script runs in *the end-point calibration mode* the purpose of which is to establish the automatic determination of the endpoint of titration. In this mode, the script tracks the area of the fuchsia-colored spot of phenolphthalein in the analyte solution. The endpoint of titration is defined as the volume of titrant corresponding to the half of the maximal area on the calibration curve (see below). Finally, the script runs in *the titration mode* where it automatically determines the volume at the endpoint of titration and prints a corresponding message to the user (Figure 2).

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195 **Figure 5.** Flow chart of the simplified CV script algorithm for automatic titration (see explanation in the text)

The CV script reads frames from the video stream as long as new frames become available (Figure 5). Each frame is analyzed by the CV algorithm to identify positions of the top, bottom, and floating marks to determine the volume of the dispensed titrant solution. The area and volume are printed on the screen. Also, the frame is processed to measure the area of the fuchsia spot in the analyte solution. The largest object which has colors in the specified range of hue, saturation, and brightness is identified. If the area of the fuchsia spot exceeds the specified threshold determined by the initial calibration of the script, a message appears to notify the user that the endpoint of titration is reached along with the volume of the dispensed titrant at which the threshold was achieved.

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The script can be run either to monitor the actual live video stream of the experiment from the webcam or to display a pre-recorded YouTube video¹³ of titration which enables a completely virtual experiment if necessary.

210 **HAZARDS**

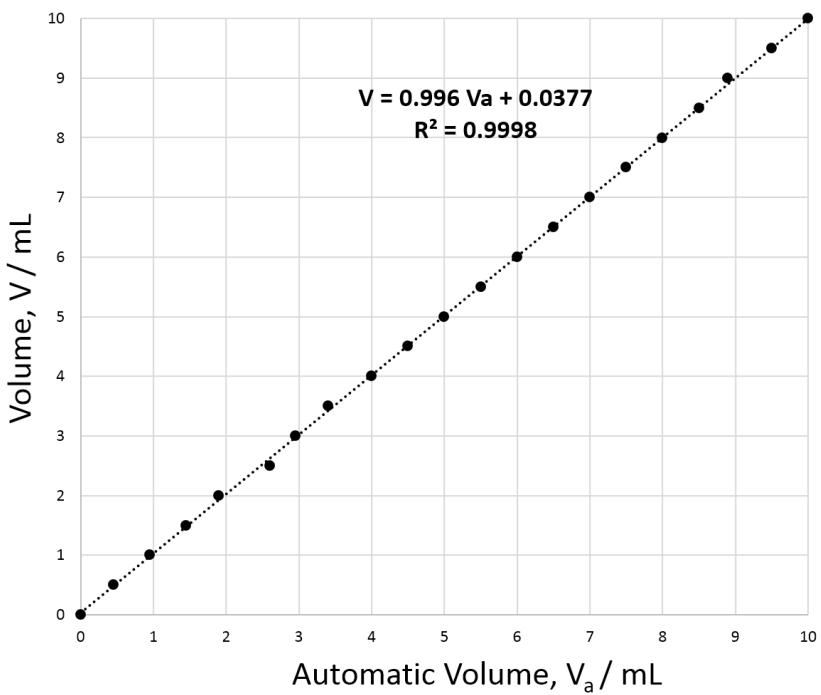
Used in the experiment, hydrochloric acid (0.1M HCl) and sodium hydroxide (0.1M NaOH) solutions are corrosive. Safety goggles, gloves, and a lab coat must be worn to prevent any skin or eye contact. Established safety protocols for regular titration experiments as determined by institutional policies must be followed.

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RESULTS AND DISCUSSION

Volumetric Calibration

Initially the volumetric calibration is performed in order to determine how accurate 220 automatic readings of the volume are. The script runs in the volumetric calibration mode (see supporting materials: S3). In order to perform the calibration, the titrant solution is dispensed manually with steps of approximately 0.5 mL and the volume (V) is manually identified using marks on the burette and recorded. Video of this stepwise process is analyzed by the CV script. The manual (V) vs. automatic volume readings (V_a) are shown 225 on a scatterplot (Figure 6). The manual vs. automatic volumetric reading demonstrates satisfactory correlation ($R^2=0.9998$). The coefficients from the calibration equation shown in Figure 6 are entered into the script to eliminate potential systematic error in volumetric readings.



230 **Figure 6.** Volumetric calibration: manually measured volume (V) vs. automatically measured volume (V_a). The linear calibration
relationship is used in the CV script.

235 A sample run is shown in Figure 7. The top panel (a) shows how the area of the fuchsia
spot changes during the run. While the analyte solution is clear during the first interval
(<100 s), the area is zero. Then, approaching the equivalence point, the value of the area
begins to fluctuate. Each drop of the titrant generates a peak in the area plot with
increasing intensity when approaching the equivalence point. Then, the color of the entire
analyte solution becomes fuchsia (~ 130 s) and the area plot levels-off at its final value
(>130 s). The average value corresponding to half of its maximal value ($\bar{A}_{1/2}$) is determined
240 during the initial calibration of the script and then used by the CV script to determine
the endpoint of titration. The lower panel (b) shows dependence of the automatically
measured volume of the dispensed titrant during the run. The slight parabolic curvature
is due to the fact that the titrant is freely dripping from the burette and the rate of flow
is decreasing as the level of the titrant in the burette (and hydrostatic pressure) decreases.
245 This effect was also observed in our previous experiment.⁴ The plot also has a level of
noise in the range of ± 0.15 mL. While the proposed setup does not require any valves or
pumps to control the flow of the titrant, the experimental setup can be modified with
addition of valves^{4,7} or a syringe pump⁶ to reduce color fluctuations. The measured value
250 of the volume is interactively displayed by the script and at the moment when the
endpoint of titration is achieved the value of the volume is recorded and indicated on the
screen as the equivalence volume (V_{eq}).

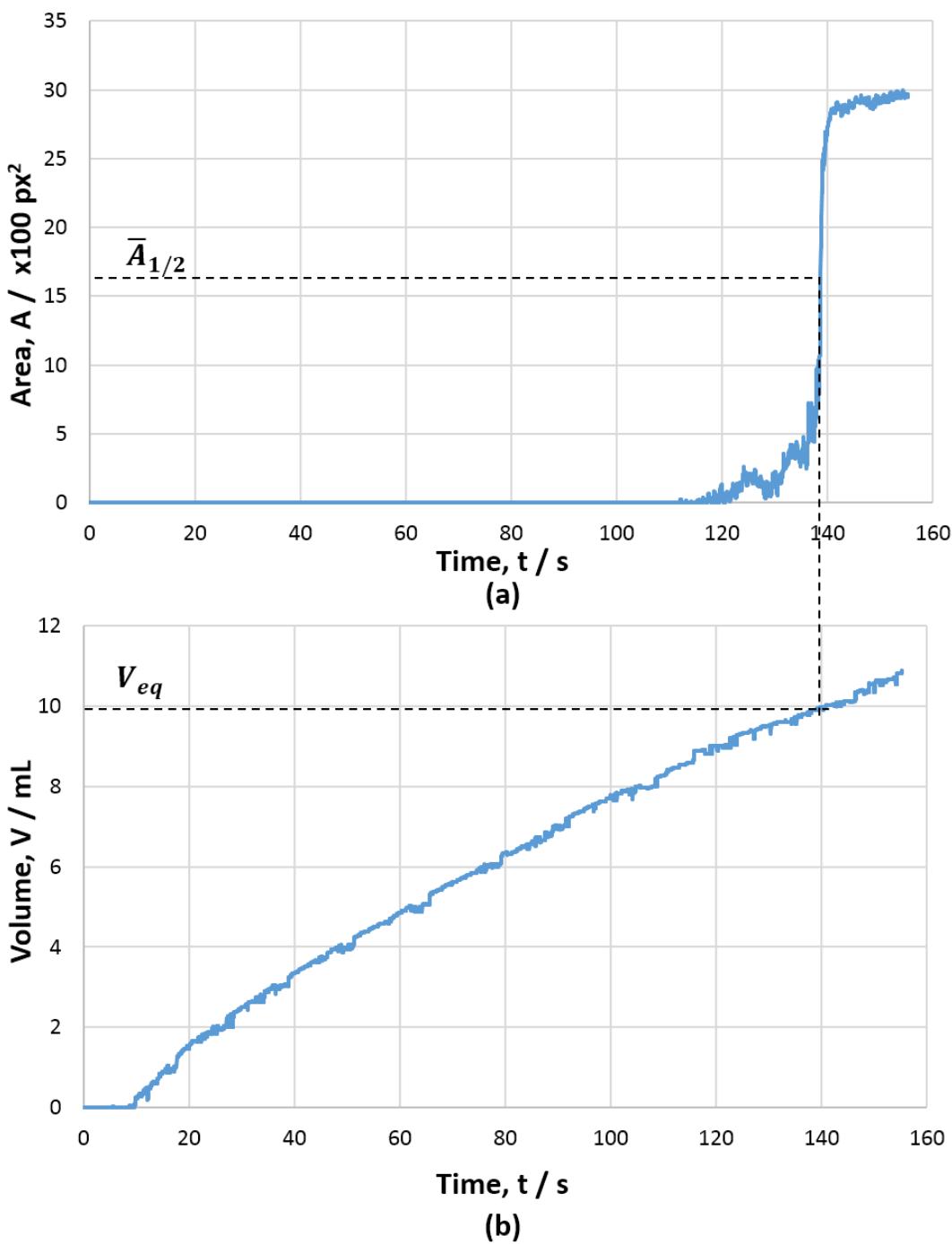


Figure 7. (a) Area (A) of the fuchsia spot and volume (V) are measured by the CV script. (b) The equivalence volume (V_{eq}) is determined automatically when the area of the fuchsia spot is reached half of its averaged maximal value ($\bar{A}_{1/2}$).

Multiple titration runs of 0.1M HCl samples with 0.1M NaOH standard titration solution were performed in order to determine accuracy of the proposed titration

technique (see Table 1). There were 10 trials with the 5 mL HCl samples and 10 runs with 10 mL HCl samples. The error analysis was performed for the 95% confidence interval of the t-distribution for the standard deviation (σ): 0.08 mL for both samples. Average equivalence volumes (\bar{V}_{eq}) are: 5.07 ± 0.18 mL (3.55%) and 9.84 ± 0.18 mL (1.81%) for 5 mL and 10 mL samples respectively. This is consistent with the concentration of the standard solutions.

Table 1. Error analysis of titration runs for 5 mL and 10 mL 0.1M HCl samples titrated with 0.1M NaOH solution. Automatically determined average equivalence volume (\bar{V}_{eq}), standard deviation (σ), absolute (ΔV) and relative (in parentheses) errors.*

\bar{V}_{eq} , mL	5.07	9.84
σ , mL	0.08	0.08
ΔV , mL	0.18 (3.55 %)	0.18 (1.81 %)

*Number of trials: 10, t-distribution value for 95 % confidence interval: 2.22814, $\bar{A}_{1/2} = 1688$ px⁻²

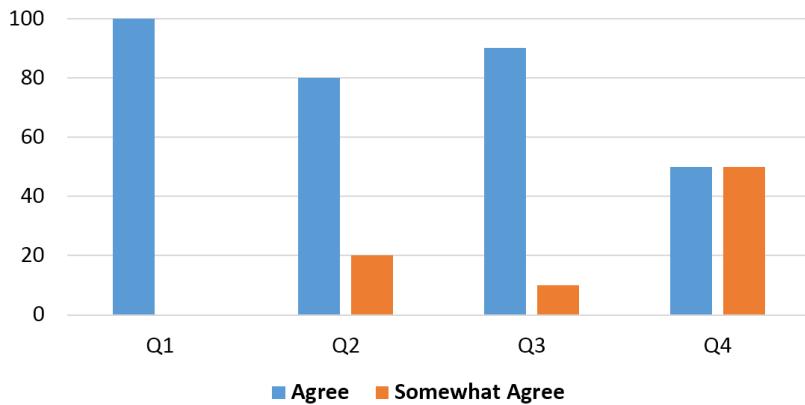


Figure 8. Students' feedback after completion of the lab: (Q1) Computer vision is a useful technology for chemists and chemical engineers. (Q2) Automatic titration well illustrated the application of computer vision in chemistry. (Q3) After completion of the lab my understanding of computer vision has increased. (Q4) After completion of the lab my interest in learning more about computer vision has increased. Options for each question: Disagree; Somewhat Disagree; Neutral; Somewhat Agree; Agree;

After completion of the lab, students were given a quick quiz comprised of four questions (Figure 8) about their opinion on the usefulness of CV applications for chemistry. Students' understanding of CV technology is based on the lab experience, as well as their interest in CV technology. As there were only 10 students in the lab section, the results are by no means statistically sound and provide mainly a perception of this lab by this small group. All students agreed that CV is a useful technology, 80% "agreed" and 20% "somewhat agreed" that it is well illustrated with the proposed experiment and 90% "agreed" and 10% "somewhat agreed" that their understanding of CV had increased. Half of the students indicated that after completion of the experiments their interest in learning more about CV technology had increased. Students were also given an opportunity to provide a comment, which half of them did. While all comments were

positive indicating students' enthusiasm for learning CV technology one student indicated that: "[I want to be] able to do the titration myself or handle reactions myself." which probably shows the student's greater interest in performing experiments in a regular classroom rather than in a virtual lab. Informal conversations with students also show their willingness to get back to in-person classes, which is understandable for the given cohort of students.

CONCLUSIONS

Computer vision platforms open new opportunities for development of novel laboratory techniques to carry out traditional as well new experiments. Also, they provide a means for on-line instruction, which was in high demand during the pandemic. The proposed methods are based on a free, open source computer vision library (e.g. CV2) and a general-purpose programming (*Python*) language which makes the lab accessible for broader communities of teachers and learners. The approach is flexible as it enables live video stream analysis as well as the analysis of a pre-recorded video of the experiment. Thus, multiple CV scripts with different calibration values and multiple CV algorithms can be tested and compared using exactly the same pre-recorded video. This feature is valuable for instructors as it makes it possible to compare outcomes of different groups of students using the same raw data, as well as improvement and validation of CV algorithms.

As it was pointed out previously students with mobility or visual impairment oftentimes have limited or no options to perform laboratory experiments.^{7-8,25} Currently, there are efforts in using robotic technology⁷⁻⁸ and computer vision²⁶ to make chemistry laboratory experiments accessible for students of all abilities. We believe that the proposed technology that enables computer-vision assisted remote execution of titration experiments will be useful for teaching students with disabilities.

Students who learn in person as well as online are exposed to a novel laboratory technique with potential to automate a wide variety of chemical techniques. However, it is noteworthy that, under normal circumstances, the virtual labs should not serve as a replacement for traditional hands-on lab instruction and may serve best as an additional activity for hybrid instruction or a snow day.

ASSOCIATED CONTENT

Supporting Information

A detailed list of software, sample color labels, experimental procedure, CV script options and usage examples, sample datasheet, and CV script source code (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

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Corresponding Author

*E-mail: dkosenkov@monmouth.edu

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