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Method of Estimation of Chemical Compounds of a Solution by Analysis of Video Images of Titration from a Semi-Automatic Approach

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Abstract

To titrate or measure a chemical species in a solution is to estimate its quantity of matter or its molar concentration in a given solution. Several methods of estimating molar concentrations of chemical species exist, the main ones being Colorimetric titration, Conductimetric titration, pH metric titration. In practice, all these methods present approximative results because the operator repeats the experiment to ensure the reliability of the results. As a consequence, we have a prolonged time of the experiment which involves a cost in reagents. Given the repetitions of the same experiment, the final result is the average of the results of each experiment. The aim of this paper is to correct this subjectivity by implementing a semi-automatic approach based on colorimetric titration. At the end of the implementation of our approach, we compared our results to those of existing techniques. These results show the reliability of the calculation by the semi-automatic method. This method of estimating the volume at equivalence is fast because it is not manual and does not involve the use of geometric measuring instruments to find the volume at equivalence. This method improves the manual calculation of the volume at equivalence used in the laboratories in school and student environment.

Keywords

Titration, Turning, Equivalence Point, Volume at Equivalence

1. Introduction

To titrate or measure a chemical species in a solution is to estimate its amount of material or its molar concentration in a given solution [1]. There are several methods for estimating the molar concentration of chemical species. Among these different methods, the main ones are:

- Colorimetric titration;
- Conductimetric titration;
- The metric pH titration.

All these methods of substance determination are of great interest in natural substance laboratories, especially in the determination of the molar concentration of the substance at equivalence [2]. However, these different methods of concentration determination are done manually, requiring colored indicators which are often inaccessible and whose zone of viability of the titrated solution remains subjective [3]. This subjectivity of the turning point makes the equivalence values unreliable. Several works have been done to optimize the values obtained at equivalence, in particular the concentration at equivalence. According to the official bulletin Hors-série N˚4 of the Ministry of National Education and the Ministry of Research of Paris, to refine the equivalence point, it is necessary to repeat the dosage a large number of times using the same colored indicator, which makes the determination very slow [4]. In order to overcome all these shortcomings and optimize the determination of concentrations at the equivalence, we have used other methods, based on the analysis and processing of sequential images integrating the evolution of the colored indicator in the titrated solution and the height of the solution. The objective of our work is therefore to propose a new approach to determine the volume at equivalence and then deduce the molar concentration of chemical species by titration. This new approach of semi-automatic determination allows to determinate the equivalence or turning point of a titrated solution. We start by presenting the related works and their limits, then present the video acquisition system and the materials used. After these different steps, we set up a semi-automatic approach. This approach consists in cutting the experimental video of a type of dosage into frames. We observed each sequential image (frame) to determine the height of the solution at the turn. After this step, we proceed to the determination of the equivalent volume and deduce the molar concentration of the titrated solution. Finally, we compared our semi-automatic approach to the manual approach currently used in high schools and colleges.

2. Related Work

According to (Laure GAUCHON in Oct. 2008), the study of titration allows to deepen the knowledge of chemical transformations in the students of the scientific classes of the second cycle. Titration is a special case of dosing; it is a chemical method that consists of gradually adding the titrating solution by pressing on Mohr's forceps. What is added to the beaker will react, so products will be

formed, but the quantity of titrated solution will decrease since it is a reagent. After a certain amount has been added, all the titrated solution will have reacted: this is called the equivalence. Equivalence is defined as the state of the system in which the titrated reagent becomes the limiting reagent whereas before equivalence the limiting reagent is the titrant. At equivalence, the volume poured will be noted VE: Vv = VE at equivalence. When we continue to add the titrant solution, there will be no more reaction because there will be no more titrated solution to react. Nakhleh *et al.*, 1993, Latifa Ouertatani *et al.*, 2008 have worked on the colorimetric titration. This approach allows to identify the equivalence thanks to the change of color of the titrated solution. In this approach we have three hypotheses of study. In the first hypothesis, we suppose that the titrated solution is the only colored one, the titrating solution and the products being colorless. In this hypothesis, we pour drop by drop the titrating solution as long as the solution is colored, and as soon as it becomes colorless we stop because we have reached the equivalence: we then look at the volume poured which corresponds to VE. In the second hypothesis, we suppose that the titrating solution is colorless, the titrated solution and the products being colored. In this second hypothesis, we pour drop by drop the titrating solution as long as the solution is colorless, and as soon as it becomes colored we stop because we have reached the equivalence: we look then at the volume poured which corresponds to VE. In the third hypothesis, we suppose that the titrating and titrated solutions are colored, while the products are colorless. In this third hypothetical, at the equivalence, the solution will be of the same color as the titrating solution. Equivalence will therefore be marked by the change in color [5]. The difficulty with this approach is that it is not precise. It is therefore difficult to make a graph unlike the pH-metric and conductimetric titrations. Naija *et al.*, 2004, Sheppard *et al.*, 2006, LE MARÉCHAL *et al.*, 2008 have worked on pH metric titration. This approach allows to follow the evolution of the pH during the reaction. In this approach, it is necessary to add a pH-metric probe with a pH-meter to read the pH according to the volume poured. Then we draw a curve representing the pH as a function of the volume poured. This approach is not very accurate, because the tangents are not drawn accurately [6].

3. Proposed Approach

3.1. Chemical Reagents and Experimental Setup

All chemicals used are of analytical quality. The solvents and reagents used were purchased commercially from Polychimie (Ivory Coast). The experimentation protocol took place in the department of Agro-Food Chemical Engineering, more precisely in the laboratory of the Chemistry Group of Water and Natural Substances (GCESNA) of the National Polytechnic Institute Houphouët Boigny (INP-HB) north of Yamoussoukro. The different devices used for our analyses are the following:

- Graduated burette (25 ml) ± 0.05 ml, T = 20˚C

- Graduated test tube (50 ml) ± 0.75 ml, T = 20˚C D = 2 cm,
- Beakers 25, 50 and 100 ml
- Graduated pipette (10 ml), ±0.1 ml, T = 20˚C
- Propipette (Pipette stick)
- Magnetic bar
- Magnetic stirrer
- The gallows
- A camera
  - Spatial resolution: 2448 × 3264 (8 M pixels)
  - Tonal resolution: 24 bits (color)
  - Color space: RGB
  - Camera model: Infinix
  - Focal length: F/2
  - Exposure time: 1/13 seconds
  - ISO sensitivity: ISO-864
  - Focal length: 4 mm
  - Image format: JPG image

The camera is fixed at 12 centimeters of the plate on a stand, a distance for a better quality of the image (sharpness) and connected to the PC by the USB port. A Windows driver allows communication between the PC and the camera. Figure 1 presents the experimental device of acquisition of sequential images.

Figure 1. Experimental materials.

3.2. Principle

The principle of our method is the automation of the volume/height reading at equivalence. Our work has allowed us to set up a semi-automatic approach. This approach consisted in setting up at:

Step 1: We proceeded to set up the experimental equipment to proceed with the titration of a solution. In this experiment, it is the titration of water by the solution of EDTA to 0.01 N with as initial volume 10 ml (V0 = 10 ml). This experimentation allowed us to acquire the video of experimentation.

Step 2: We proceeded to the decomposition of this video of experimentation in several sequential images illustrated in example by the following images (see Figure 2).

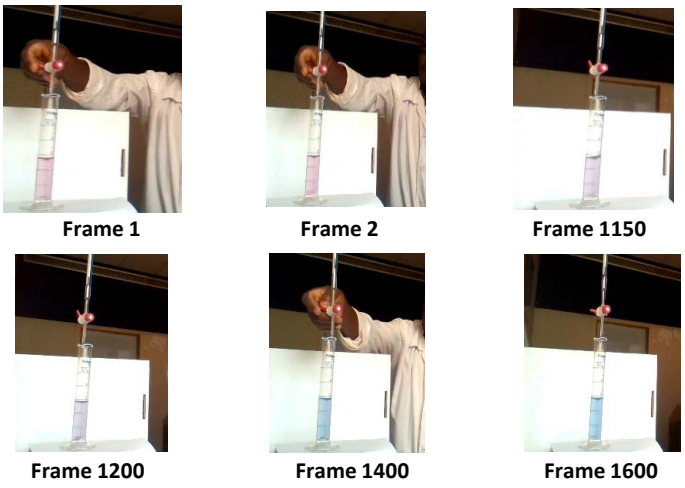

Figure 2. Some experimental images from the acquisitions database.

Step 3: These sequential images allowed us to build an image database.

For Frame 1 we made several height measurements and calculated the average height as shown in Table 1.

Table 1. Experiment 1.

Frame	Measurement of height H in pixels	Indicator	Result
1	124 123 123.5		No turn
Average height in pixels	**123.5**		

For Frame 2 we made several height measurements and calculated the average height as shown in Table 2.

Table 2. Experiment 2.

Frame	Measurement of height H in pixels	Indicator	Result
2	125 124.5 124		No turn
Average height in pixels	**124.5**		

For the Frame 1200 we made several height measurements and calculated the average height as shown in Table 3.

Table 3. Experiment 1200.

Frame	Measurement of height H in pixels	Indicator	Result
1200	128 127.5 127		Turn
Average height in pixels	**127.5**		

From the above, we have constituted an acquisition database with the 3030 frames. This database is illustrated by Table 4.

Table 4. Acquisitions database.

Frame	Measurement of height H in pixels	Indicator	Result
1	123.5		No turn
2	124.5		No turn
100	124.5		No turn
1000	126		No turn
1100	126.5		No turn
1200	**127.5**		Turn
1400	128		No turn
1600	129		No turn

Continued

…….	……	…….	…….
3030	129.5		No turn

Step 4: We measure the height of each image. If the color of the titrated solution remains unchanged, we continue to measure a new height. However, if the color of the titrated solution changes state then we are at the equivalence point. This leads us to record the height of the titrated solution. By analogy this semi-automatically determined height allows us to determine the volume at the equivalence point.

Step 5: We deduce the concentration of the titrated solution.

This whole process is summarized by the algorithm shown in Figure 3.

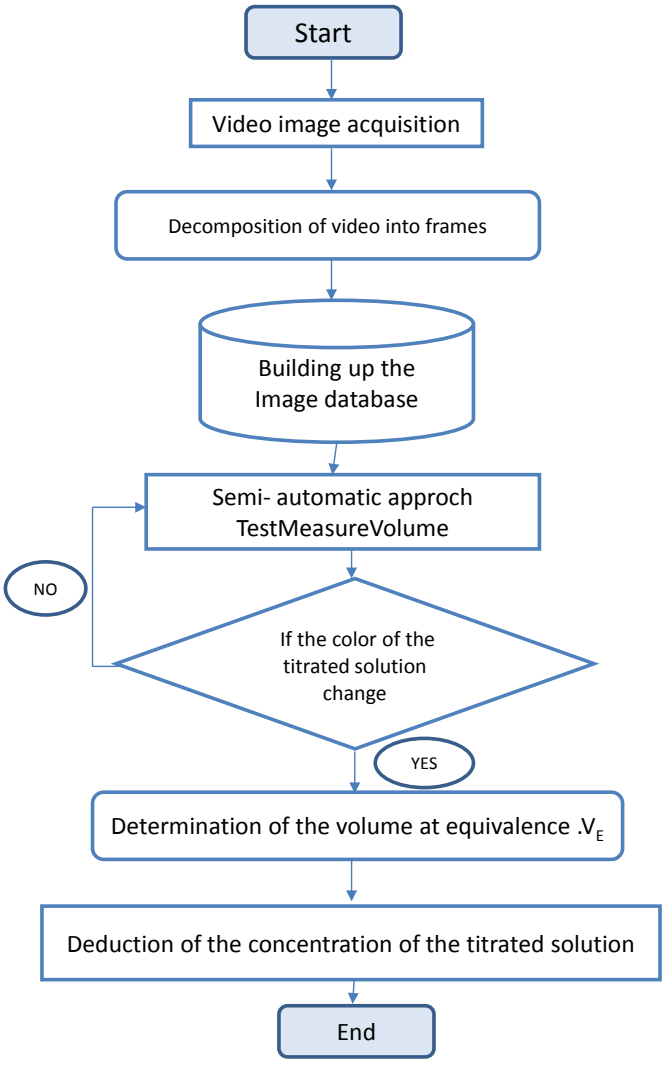

Figure 3. Semi-automatic approach.

4. Results and Discussion

The semi-automatic technique implemented in the Matlab software allowed us to measure the different heights of the titrated solution. When we visually observe that there is a change in color of the titrated solution, our approach measures with precision the height. We are therefore at the turn. This height determined at the turn represents the equivalent height (h_e). This height is expressed in pixels. By observing our experiment representing the titration of water by the EDTA solution at 0.01 N, we have the following explanation:

In the initial state, we have the Initial Volume named V_0 = 10 ml corresponding to the initial volume of the solution containing the titrated species. According to **Table 4**, representing the acquisition database, we have Frame 1 corresponding to the initial state of our data. In Frame 1, we have the initial height named h_1 = 123.5 pixels. In the same base, we have Frame 1200 which determines the equivalent height named h_e = 127.5 pixels. At this height we have a change of state of the titrated solution. This change of state corresponds to the turn. From this height h_e, we determine the Volume at Equivalence. To determine the volume at equivalence V_e we use the mathematical technique of the rule of three.

$$\begin{array}{c} h_0 \rightarrow V_0 \\ \times \\ h_e \rightarrow V_e \end{array}$$

This rule of three, allows us to have the following formula:

$$V_e = \frac{V_0}{h_0} * h_e \tag{1}$$

Note

$$\alpha = \frac{v_0}{h_0} \tag{2}$$

α is expressed in ml/pixel.

The general formula becomes

$$V_e = \alpha * h_e \tag{3}$$

Applying this to our values we have:

$$V_e = \frac{10}{123.5} * 127.5$$

$$V_e = 10.32 \text{ ml}$$

with

V_e: Volume at equivalence

α: Steering coefficient

h_e: Equivalent height

V_0: Initial volume

From this calculation, the volume at equivalence (V_e :) is 10.32 ml. Comparing this result with the result of the same experiment done manually as shown in

Table 5.

Table 5. Manual experimentation table for colorimetric titration.

Solution	Different Experiences	Volume of titrant solution poured in ml	Volume of the titrated solution (water)	Volume of the titrated solution at equivalence	Concentration of the EDTA titrant solution
Total Hardness	Experience 1	0.6	10	10.6	0.01N
	Experience 2	0.6	10	10.6	
	Experience 3	0.6	10	10.6	
	Experience 4	1.2	10	11.2	
	Experience 5	1	10	11	
	Experience 6	1.1	10	11.1	
	Experience 7	1.1	10	11.1	
	Experience 8	1.1	10	11.1	
	Experience 9	1.1	10	11.1	
	Average number of readings	**0.93**	**10.00**	**10.93**	

Table 5 shows the results of the handwork experiments. We can group these experiments into four groups.

- Group 1 consists of experiments 1, 2 and 3;
- Group 2 consists of experiment 4;
- Group 3 consists of experiment 5;
- Group 4 consists of experiments 6, 7, 8 and 9.

In group 1, the volume of the titrant solution poured in is 0.6 ml and the volume of the initial titrant solution is 10 ml.

This allows us to obtain at the turn or at the equivalence a titrated solution of volume 10.6 ml.

Using the same approach in group 2, the volume of the standard solution at equivalence is 11.2 ml.

According to the same approach in group 3, the volume of the standard solution at equivalence is 11 ml.

According to the same approach in group 4, the volume of the titrated solution at equivalence is 11.1 ml.

From the above we have calculated the average volume of the titrated solution at equivalence to be 10.93 ml.

From Table 6 and Figure 4, we observe that the volume of the titrated solution in our experiment (semi-automatic method) is 10.32 ml and remains constant, unchanged whatever the experiment.

On the other hand, with the traditional method, the volume of the titrated solution at the equivalence varies according to the experiments. This table shows the differences between the values measured with the traditional method and the semi-automatic method (our method).

Table 6. Experimental table 1.

Different Experiences	Volume of the titrated solution at equivalence (Manual method)	Volume of the titrated solution at the equivalence of our experiment (Semi-automatic method)	Distortion in ml
Experience 1	10.6	10.32	0.28
Experience 2	10.6	10.32	0.28
Experience 3	10.6	10.32	0.28
Experience 4	11.2	10.32	0.88
Experience 5	11	10.32	0.68
Experience 6	11.1	10.32	0.78
Experience 7	11.1	10.32	0.78
Experience 8	11.1	10.32	0.78
Experience 9	11.1	10.32	0.78
Average value of reading	**10.93**	**10.32**	**0.61**

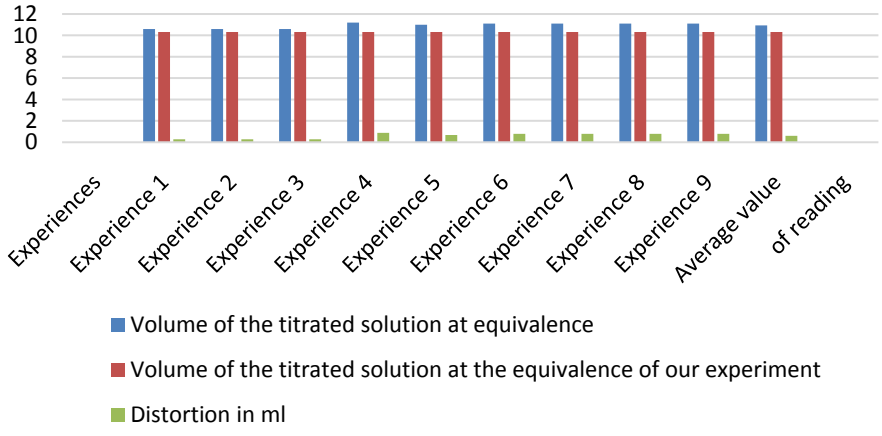

Figure 4. Comparative study of manual and semi-automatic methods in ml.

In this section, we will convert the equivalent volume to equivalent height using the following formula:

$$h_n = \frac{1}{\alpha} * v_n \tag{4}$$

Table 7 and Figure 5 represent the results of the handwork experiments with equivalent heights expressed in pixels.

We can group these experiments into four groups.

- Group 1 consists of experiments 1, 2 and 3;
- Group 2 consists of experiment 4;
- Group 3 consists of experiment 5;
- Group 4 consists of experiments 6, 7, 8 and 9.

Table 7. Experimental table 2.

Different Experiences	Height in pixels (Manual method) $h_n = \frac{1}{\alpha} * v_n$	Equivalent height (H_e) in pixels	Distortion in pixels
Experience 1	130.91	127.5	**3.41**
Experience 2	130.91	127.5	**3.41**
Experience 3	130.91	127.5	**3.41**
Experience 4	138.32	127.5	**10.82**
Experience 5	135.85	127.5	**8.35**
Experience 6	137.09	127.5	**9.59**
Experience 7	137.09	127.5	**9.59**
Experience 8	137.09	127.5	**9.59**
Experience 9	137.09	127.5	**9.59**
Average value of reading	**134.99**	**127.5**	**7.49**

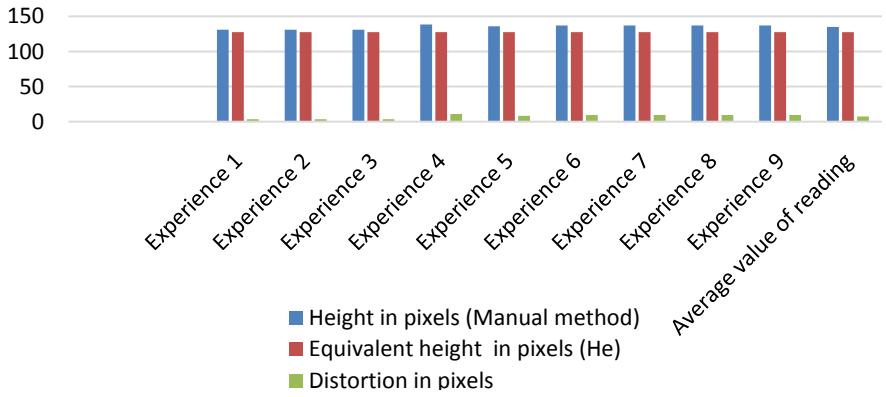

Figure 5. Comparative study of manual and semi-automatic methods in pixels.

In group 1, the equivalent height obtained using the formula h_1 is 130.91 pixels.

According to the same approach in group 2, the equivalent height obtained using the formula h_2 is 138.32 pixels.

According to the same approach in group 3, the equivalent height obtained using the formula h_3 is 135.85 pixels.

According to the same approach in group 4 the equivalent height obtained using the formula h_4 is 137.09 pixels.

From the above, we calculated the average height of the titrated solution at the equivalence which is 134.09 pixels.

From Table 7, we observe that the height of the titrated solution in pixels of our experiment (semi-automatic method) is 125.5 and remains constant, unchanged for all experiments.

On the other hand, with the traditional method, the volume of the titrated solution at the equivalence varies according to the experiments. This table allows

us to observe the differences between the values measured with the traditional method and the semi-automatic method (our method).

In sum, we note that the work of Latifa Ouertatani *et al.*, 2009 lacks appreciation of the reading of volumes during the change of colours.

For the determination of the Volume at Equivalence, since this is manual, Latifa Ouertatani *et al.* performed the same experiment several times in order to determine the average volume at equivalence. This volume at equivalence represents the average of all volumes at equivalence determined during the different experiments. In terms of time management their approach is not optimal compared to our semi-automatic approach. Secondly, their approach results in reagent waste. Our approach is optimal in terms of time management and efficient in reagent consumption. A single experiment can accurately determine the volume at equivalence.

Comparing the results of the two experiments, we observe Table 8.

Table 8. Comparative table of the two methods.

Methods	C_a	VE
MANUAL	0.01	10.93
SEMI AUTOMATIC	0.01	10.32

The term:

C_a : the molar concentration of the titrant solution.

V_a : the volume de la solution titrante.

V_e : the volume at equivalence.

This table allowed us to have the following graph illustrated by Figure 6:

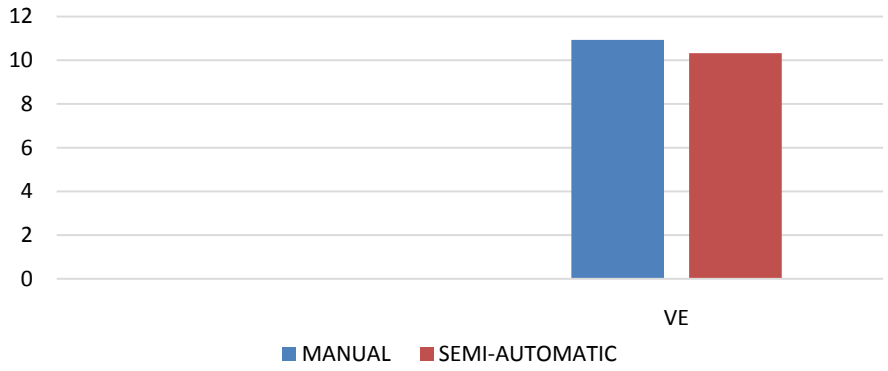

Figure 6. Comparison of the two methods.

From Figure 6, we observe that our approach reaches the Volume to Equivalence before the traditional approach. This leads to the conclusion that our semi-automatic approach is efficient and effective.

This approach will optimize the calculation of the determination of the volume at equivalence by students in science classes.

This method is simple and very efficient to determine with precision the end

point of the reaction using volumetric measurements and colorimetric titration.

5. Conclusions

This article describes the method of estimating chemical compounds in a solution by analysis of video titration images.

Titrating or dosing a chemical species in a solution means estimating its amount of material or its molar concentration in the given solution. There are several methods for estimating the molar concentration of chemical species. Among these different methods, the main ones are

- Colorimetric titration;
- Conductimetric titration;
- Ph-metric titration;
- Potentiometric titration;
- Volumetric titration.

All these methods of substance determination are of great interest in natural substance laboratories but also in our high schools and colleges, especially in the determination of the molar concentration of the titrated solution at the equivalence.

However, these different methods of determining the concentration are done manually, requiring coloured indicators that are often inaccessible and whose colour change zone of the titrated solution remains subjective.

This subjectivity of the colour change zone makes the equivalence values unreliable. Several works have been carried out to optimise the said equivalence values, in particular the volume at equivalence and the deduction of the molar concentration at equivalence.

The work of Latifa Ouertatani *et al.*, 2009 in order to refine the equivalence point, repeated the determination a large number of times using the same coloured indicator, which makes the determination very slow and often costly in reagents.

In order to overcome all these shortcomings and optimise the determination of the volume at the equivalence point, we used a method based on the analysis and processing of sequential images integrating the evolution of the coloured indicator in the titrated solution and the height of the said solution.

Our work consisted in proposing a new approach called semi-automatic approach for the determination of the volume at equivalence and proceeded to the deduction of the molar concentration of chemical species by titration.

We have carried out various titration experiments and the video images of these experiments are produced with a colour cmos camera. The experimental results of the volumes poured of the titrating solution are measured.

A semi-automatic calculation of the pouring volumes by processing the acquired video images gives results very close to the results of the manual approach.

Furthermore, our next challenge is to propose a second approach which consists of the determination of the equivalence point of a chemical solution based

on the colorimetric titration by the so-called automatic method.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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