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RESEARCH ARTICLE

METHOD FOR IDENTIFYING THE EQUIVALENT FRAME OF A SOLUTION BY ANALYZING TITRATION VIDEO IMAGES USING AN AUTOMATIC APPROACH

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Abstract

Determination of equivalence in inorganic chemistry can be achieved by various methods, such as colorimetric titration, conductimetric titration and pH-metric titration. However, these traditional methods often require repetition to guarantee reliable results, increasing the time and cost of the experiment. In response to this limitation, some authors have suggested a semi-automatic approach based on colorimetric titration, although this also has subjective aspects. The aim of this article is to propose a new method based on intuitive observation to identify the equivalent frame in a titration video. This approach relies on the use of the KNN classifier to automate the detection of the reference frame within a predefined confidence interval. To facilitate this automation, a dataset was built up from experiments at the Groupe Chimie de l'Eau et Substances Naturelles (GCESNA) laboratory at the Institut National Polytechnique HouphouëtBoigny (INP-HB).The performance of the KNN algorithm was effectively assessed by evaluating it against the performance indicators of precision, recall and F-measure. The results obtained are as follows: Precision: 92.2%, Recall: 91.7% and F-measure: 92.0%. These experimental results demonstrate the effectiveness of the KNN algorithm in frame classification.

Introduction:-

The determination of equivalence in inorganic chemistry holds paramount significance across various scientific and industrial domains. Traditional methods such as colorimetric titration, conductometric titration, and pH-metric titration [1][2] have long been employed for this purpose. However, these conventional approaches come with notable limitations, particularly in terms of experimental duration and costs associated with repetitive experiments [1][2].To overcome these constraints, some alternatives have been proposed, including a semi-automated approach based on colorimetric titration [3]. Nonetheless, it is crucial to emphasize that even this alternative method is not devoid of subjectivity, introducing a level of uncertainty into the obtained results. The objective of this article is to introduce an innovative approach for identifying the equivalence frame in the titration process. This method relies on an intuitive observation focused on identifying the equivalence frame in a video sequence used for titration. To enhance the efficiency of this identification, the article suggests employing a K-nearest Neighbours (KNN) classifier to automate the detection of the reference frame, based on a predefined confidence interval [4]. The performance of the KNN algorithm was assessed using standard metrics such as precision, recall, and F-measure. The results

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demonstrate the effectiveness of this approach in determining equivalence in inorganic chemistry, offering a promising alternative to traditional methods. For a comprehensive understanding of the methodology employed, this article is structured into three major parts. Firstly, the first part extensively presents the materials and methods used. Subsequently, the second part discusses related works, situating this approach within the context of current research. Finally, the third part elucidates the steps and choices made in the proposed approach, providing a complete perspective on the adopted methodology.

Related Work:-

According to (Laure GAUCHON et al ,2008), the study of titration proves to be an opportunity to deepen the knowledge of chemistry students, particularly those in the scientific classes of the second cycle [5]. Titrations represent a chemical method involving the gradual addition of a known concentration titrant solution to an unknown concentration titrated solution. Observation of the reaction environment reveals that the titrant completely reacts with the titrated substance, thus reaching the equivalence point.In summary, at equivalence, we have Vv = VE, where the poured volume is denoted as Vv, and VE represents the equivalent volume.

(Nakhleh et al ,1993), as well as (Latifa Ouertatani et al, 2008), explored colorimetric titration, basing their approach on the color change of the titrated solution to identify equivalence[6]. Three essential hypotheses arise from this approach.In the first hypothesis, the premise is that the titrated solution is the only one colored, while the titrant solution and products are colorless. In this scenario, titration is performed, and the process is halted as soon as the titrated solution becomes colorless, indicating the achievement of equivalence. The volume poured at this stage is then recorded as the equivalent volume, denoted as VE. In the second hypothesis, the assumption is that the titrant solution is colorless, while the titrated solution and products are colored. In this configuration, titration is repeated, and the process is stopped as soon as the titrated solution takes on a colored hue, marking equivalence. The poured volume at this stage is once again recorded as the equivalent volume, VE. In the third hypothesis, the preconceived idea is that both the titrant solution and the titrated solution are colored, while the products remain colorless. At equivalence, the solution will take on the color of the titrant solution, allowing the identification of equivalence through the color change [7]. An inherent difficulty in this approach lies in its lack of precision, making the creation of a graph challenging, unlike pH-metric and conductimetric titrations.

(Naija et al ,2004), (Sheppard et al, 2006), and (Maréchal et al,2008) have investigated pH-metric titration. This approach allows for monitoring the pH behavior during a reaction. In this method, a pH electrode placed in a pH meter is used to record the pH as a function of the volume added[8]. Based on the recorded data, a graph is plotted to illustrate the pH evolution concerning the added volume. However, this approach has shortcomings primarily associated with the drawing of tangents.

Materials and Methods:-

Chemical Reactants:

All chemicals employed in this study are of analytical grade. Solvents and reagents were procured commercially from Polychimie (Côte d'Ivoire). The experimental protocol was conducted at the Department of Training and Research in Chemical and Agro-Food Engineering, specifically within the Laboratory of Water Chemistry and Natural Substances (GCESNA) at the National Polytechnic Institute HouphouëtBoigny (INP-HB) in Yamoussoukro. The specific products utilized for this purpose are detailed in Table 1 below.

Table 1:- Products of the experiment.

Designation	Molar Mass (g/mol)	chemical formulas	utilization
Sodium Hydroxides	40	NaOH	Titrated Solution
Sulfuric Acids	98,08	H2SO4	Titrated Solution
Acetic Acid	60	CH3COOH	Titrated Solution

Experimental apparatus

To establish the experimental database, it was observed that the use of various devices and instruments was crucial. Among these elements are:A graduated burette of 25 mL with a precision of ±0.05 mL, maintained at a temperature of 20°C. A graduated measuring cylinder of 50 mL with a precision of ±0.75 mL, also maintained at a temperature of 20°C, and characterized by a diameter of 2 cm. Beakers of various capacities, including 25 mL, 50 mL, and 100 mL. A graduated pipette of 10 mL, with a precision of ±0.1 mL, at a temperature of 20°C.

A pipetting aid (Pois à pipeter) to facilitate the pipetting process. A magnetic stirring bar used in conjunction with a magnetic stirrer to promote reactions. A stand, an essential device for suspending objects during manipulations.

A PXW-Z100 camera equipped with CMOS Exmor R™ sensors compatible with a 4K resolution (4096 x 2160) at 60 fps or 50 fps, while maintaining a weight of less than 3 kg. The PXW-Z100 uses the XAVC recording format, characterized by the efficient MPEG-4 AVC/H.264 compression method, allowing for videos in HD (1920 x 1080), QFHD (3840 x 2016), and 4K (4096 x 2160). Image sampling is at 10 bits 4:2:2, with an intra-frame system that compresses each individual image at a respective maximum bit rate of 500 Mbit/s or 600 Mbit/s during 4K recordings at 50 fps or 60 fps, and 223 Mbit/s during HD recordings at 50 fps or 60 fps.The camera was mounted on a tripod at an optimal distance to ensure superior image quality, and it was connected to the PC via the USB port, as illustrated in Figures 1 and 2 below.

Figure 1:- Diagram of the experimental digital image acquisition setup.

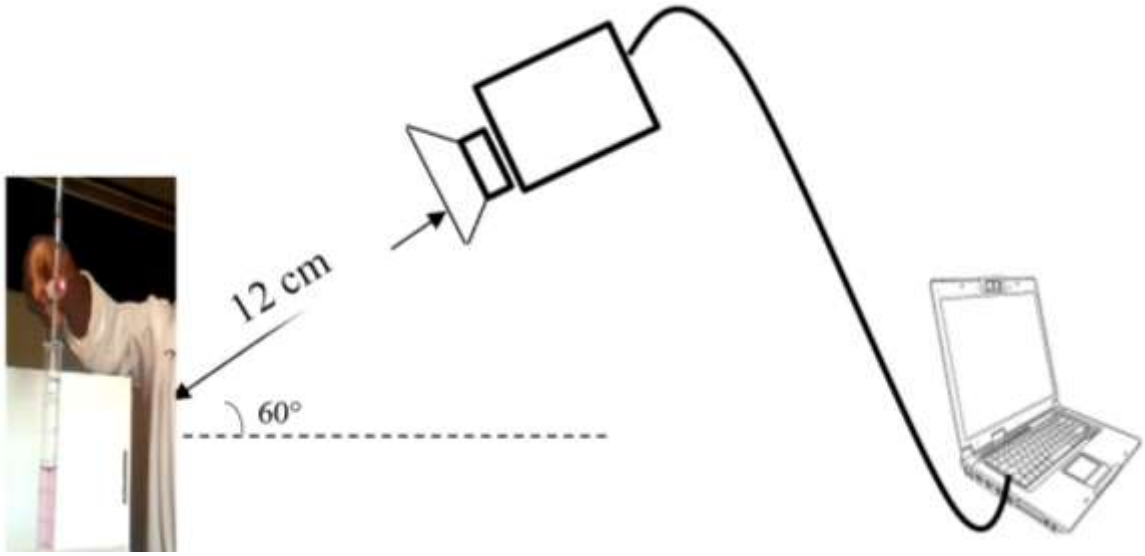
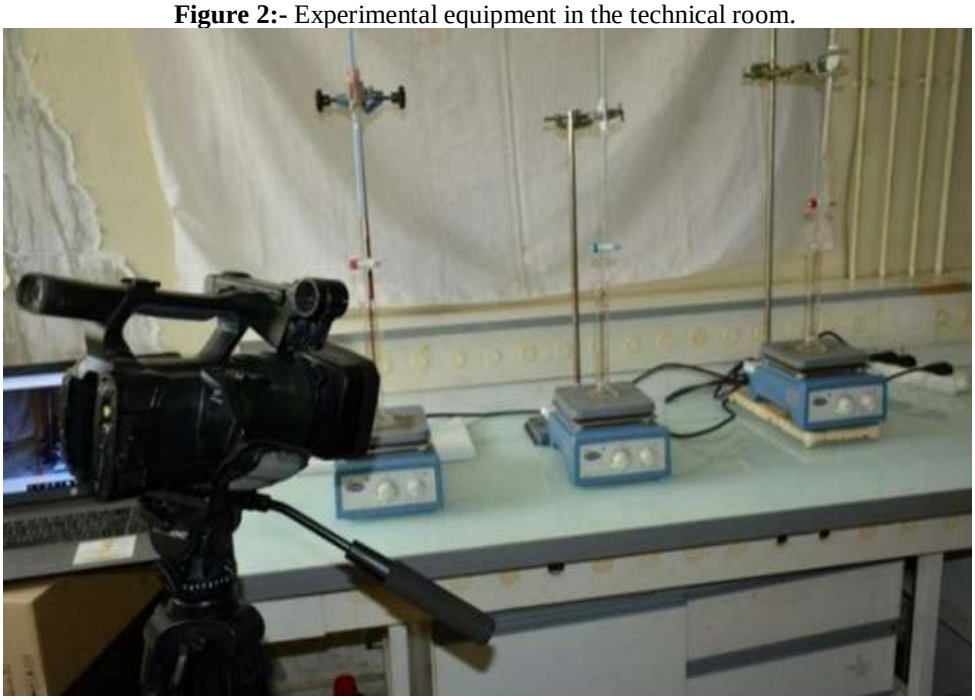


Figure 2:- Experimental equipment in the technical room.



Proposed Approach

To determine the reference frame and precisely locate the equivalence frame, eight (08) detailed steps are encompassed in the presented approach. Additionally, the process's flowchart and algorithm have been developed in subsections within the subsequent section.In this research, an automated approach is deployed to identify the reference or decision frame, necessitating the selection of a region of interest. The process unfolds through the following stages:

Step 1: Video Titration Acquisition

Initiating the process involves recording the titration video, capturing the ongoing chemical procedure. This is achieved using appropriate video capture equipment, ensuring an accurate representation of the titration sequence.

Step 2: Decomposition of the Video into Image Sequences or Frames

The video is subsequently broken down into a sequence of static images, termed frames. This decomposition allows for discrete analysis of each titration moment, simplifying the subsequent manipulation and processing of visual data.

Step 3: Determination of the Starting Frame (Initial Acquisition Point through Appraisal)

Essential to the process is the subjective determination of the starting point for image acquisition.

Step 4: Identification of a Region of Interest

A region of interest is defined, concentrating the analysis on a specific segment of the video. This selection is guided by distinct titration characteristics, thereby optimizing the identification algorithm.

Step 5: Identification of the Reference Frame via the K-nearest Neighbors (KNN) Algorithm

The KNN algorithm is employed to automate the detection of the reference frame within the pre-established region of interest.

Step 6: Identification of the Decision Frame from Previously Recorded Reference Frames

Comparison of previously recorded reference frames with current frames is carried out. This comparative analysis aims to identify the current frame that most aligns with previously recorded decisions, consequently determining the decision frame in the new sequence.

Step 7: Saving the Results

The outcomes of the analysis, including reference and decision frames, are archived for future reference. This step ensures the traceability of analyses and simplifies the reuse of data for subsequent studies or comparisons. The approach amalgamates video acquisition techniques, image processing, and the utilization of a machine learning algorithm (KNN) to automate the identification of reference and equivalence frames in the titration context.

Through this approach, an algorithm has been developed, titled "IdFrameEquivalente (IFE)." Its aim is to automate the process of identifying reference and equivalence frames in the context of titration.

Algorithm: IdFrameEquivalente (IFE)

```
Variables
        Video : video
        Frame_depart, zone_interet, frame_decision, frame_reference: image
        Zone_interet, frames_reference_precedentes: image

Begin

        // Step 1: Titration Video Acquisition
        Video = RECORD_TITRATION_VIDEO ()
        // Step 2: Decomposition of the Video into Image Sequences or Frames
        frames = DECOMPOSE_VIDEO_INTO_FRAMES(video)
        // Step 3: Determination of the Starting Frame (Initial Acquisition Point through Appraisal)
        frame_depart = CHOOSE_STARTING_FRAME(frames)
        // Step 4: Identification of a Region of Interest
```

```
    zone_interet = SELECT_REGION_OF_INTEREST(frame_depart)
    // Step 5: Identification of the Reference Frame via the K-nearest Neighbors (KNN) Algorithm
    frame_reference = IDENTIFY_REFERENCE_FRAME(zone_interet, frames)
    // Step 6: Identification of the Decision Frame from Previously Recorded Reference Frames
    frames_reference_precedentes = LOAD_PREVIOUS_REFERENCE_FRAMES()
    frame_decision = IDENTIFY_DECISION_FRAME(frame_reference, frames_reference_precedentes)
    // Step 7: Saving the Results
    SAVE_RESULTS(frame_reference, frame_decision)
End
```

Results and Discussion:-

The implementation of the IdFrameEquivalente (IFE) algorithm was carried out using Matlab. Fifteen (15) experiments were conducted for each type of titration. Out of these fifteen experiments, 80% were utilized to construct our learning database, while the remaining 20% were designated for test data. The aim of these experiments is to automatically identify the reference frame for the equivalence zone, where the color change occurs. This experimentation facilitated the creation of a titration video database, decomposed into sequential image sequences. Executing the IFE algorithm requires selecting an image sequence as the starting frame for titration, as depicted in Figure 3 below. Starting from Figure 3, the selection of the region of interest was carried out using the segmentation technique, pixel classification, and parameter calculation, as illustrated in Figures 4 and 5.

Figure 3:- Starting Image.

Figure 4:- Cropping.

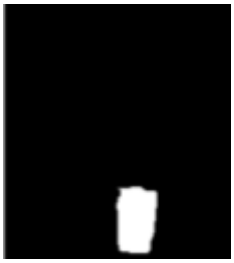


Figure 5:- Selected Zone.

Training phase

To construct the reference database, Table 2 was developed using titration videos for the training phase. The colorimetric titration method was employed, enabling the determination of the concentration of a substance in a solution by observing a color change resulting from a chemical reaction. Throughout the training phase, the following steps were taken:

Step 1: Preparation of the solution.

Step 2: Addition of a colored indicator to the titrated solution, chosen so that the color change coincides with the equivalence point of the chemical reaction.

Step 3: Titration - adding the titrant drop by drop while gently stirring. The colored indicator reacts gradually with the titrant, causing a color change in the solution.

Step 4: Color change - careful observation of the color change. As equivalence approaches, the color change becomes more evident.

Step 5: Equivalence point - the stage of titration where the chemical reaction is complete.

Step 6: Identification of the equivalence point - precise observation of the color change of the colored indicator, usually stable after a slight overdosing of the titrant.

In this specific case, with the experiment involving Calcium Hardness and the titration of water with EDTA, the equivalence point is marked by the blue color of bromothymol.Following these steps, the following table2 was compiled, representing the values of the experiments, the starting frame, the chosen frame, video format, the number of frames, the frame rate, the maximum deviation, the reference frame in the equivalence zone, and the confidence interval.

Table 2:- Values of the experiments.

Experiences	Starting frames	Selected frame	Video format	Number of frames	Frame rate in seconds	MaxEcart	Reference frame in the equivalence zone	Confidence interval	Number Predicted equivalence factor
Experience 1		1	RGB24	3000	29.95	15	1573	[1543 ;1602]	1573
Experience 2		1	RGB24	3500	30	16	1821	[1721 ;1851]	1821
Experience 3		1	RGB24	3800	50	50	1200	[1150 ;1250]	1200
Experience 4		1	RGB24	3600	30	16	1821	[1721 ;1851]	1821
.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

Identifying the equivalence frame from the confidence interval

The confidence interval, serving as a measure of estimation precision, delineates the range of values within which the estimation is likely to fall. The identification of the equivalence frame was accomplished using the K-nearest neighbors (KNN) algorithm. RGB images were digitized by calculating the red, green, and blue components of each pixel for KNN application. Throughout this process, KNN classified the frames by selecting the K nearest neighbors of a new point, determined by calculating the distance between frames within the confidence interval. The nearest frame was employed to predict the equivalence frame. The experimental data, comprising 3000 images of 32x32 pixels, underwent preprocessing involving frame normalization (division by 255) and conversion into vectors by concatenating the red, green, and blue components. The optimal value for K was established at 5. As per Table 3, the confidence intervals, being narrow, indicate a high precision of estimations. It is crucial to emphasize that the confidence interval is based on the assumption of a normal distribution. Concluding these experiments, we present an overview of the equivalence frame, as illustrated in Figure 6.

Figure 6:- Equivalent frame.

Leveraging the KNN technique in image analysis, we have the following table3

Table 3:- Result of the training phase.

Experiences	Confidence interval	Equivalence frame	RGB data within the confidence interval
Experience 1	[1543 ;1602]	**(0, 1, 254)**	[0, 0, 254, 256]
Experience 2	[1721 ;1851]	**(0, 2, 253)**	[0, 0, 253, 255]
Experience 3	[1150 ;1250]	**(0, 3, 252)**	[0, 0, 252, 254]
Experience 4	[1721 ;1851]	**(0, 4, 251)**	[0, 0, 251, 253]
Experience 5	[1150 ;1250]	**(0, 5, 250)**	[0, 0, 250, 252]
Experience 6	[1543 ;1602]	**(0, 6, 249)**	[0, 0, 249, 251]
Experience 7	[1791 ;1851]	**(0, 7, 248)**	[0, 0, 248, 250]
Experience 8	[1150 ;1250]	**(0, 8, 247)**	[0, 0, 247, 249]
Experience 9	[1791 ;1851]	**(0, 9, 246)**	[0, 0, 246, 248]
Experience 10	[1150 ;1250]	**(0, 10, 245)**	[0, 0, 245, 247]

The same study approach was applied to the following titrations:
- Classic hardness titration;
- Chloride ions titration;
- Acidimetric titration;
- Magnetic titration.

The performance of the KNN algorithm was assessed using precision, recall, and F-measure. The obtained results are as follows:

Precision (or Precision): Precision is the percentage of correctly classified frames, calculated using the formula:

$$Precision = \frac{TP}{TP + FP}$$

TP: True Positives
FP: False Positives

Recall (or Recall): The percentage of frames from the real class correctly classified is determined by the formula:

$$Rappel = \frac{TP}{TP + FN}$$

FN: False Negatives

The F-measure is a combination of precision and recall. It is calculated using the formula:

$$\mathrm{F-mesure} = 2 * \frac{Recall * Precision}{Recall + Precision}$$

The results of these performance indicators are as follows:
Precision: 92.2%
Recall: 91.7%
F-measure: 92.0%

The pedagogical contributions of researchers L. Ouertatani, A. Dumon, M. B. Nakhleh, J. S. Krajcik, Naija R., and J.-F. Le Maréchal, N. Rym, in the field of chemistry have addressed various aspects related to the learning of acid-base reactions and titrations. Their works have scrutinized teaching methods, obstacles encountered by students, and pedagogical strategies aimed at improving the understanding of specific concepts in these domains. The results of their research have provided significant insights into the effectiveness of educational approaches in these particular contexts. Simultaneously, the present research introduces an innovative methodology for the automated identification of the equivalent frame of a solution through the analysis of titration video images. In comparison with the previous works of the mentioned researchers, this approach stands out for its specific focus on automating the process of identifying the equivalent frame, leveraging modern techniques in image analysis and machine learning. Previous works, while exploring various aspects of learning acid-base reactions and titrations, give way to an advanced methodology in this study, centered on addressing challenges related to the precise identification of the equivalent frame. The use of algorithms such as K-nearest Neighbors (KNN) and the application of a semi-automatic approach characterize this contribution, thus paving the way for a constructive discussion on the significant advancements brought about by this new methodology.

Conclusion:-

The present research has made an innovative contribution to the automation of equivalent frame identification in the context of titration through video image analysis. In comparison with previous works, this approach has stood out for its specific focus on utilizing modern techniques in image analysis and machine learning, particularly the application of the K-nearest Neighbors (KNN) algorithm. The obtained results have demonstrated the effectiveness of this methodology, with promising precision, recall, and F-measure. The automation of the equivalent frame identification process offers significant prospects for improving the efficiency of titration experiments and facilitating the understanding of associated concepts.

As for future perspectives, it would be interesting to extend this methodology to other types of titrations and chemical systems. The integration of advanced machine learning and image analysis techniques could further enhance the precision of identification. Additionally, exploring solutions to handle variable experimental conditions and adapting the algorithm to specific contexts could be promising research directions. Ultimately, this approach paves the way for significant developments in the field of titration analysis automation and optimization of experimental procedures in chemistry.

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