

Determination of Aluminum (III) by Alizarin DYE in Pharmaceutical Sample and Aqueous Solution

Zaid Noor Obaid Al-Husseini^{1*}, Maiada Abdaula Adnan², Maha Abid AL-Hussain³

¹ Babylon administration of education.

² Biochemistry Department Alzahraa, College of Medicine, University of Basrah, Iraq

³ Department of Applied Marine Science, Faculty of Marine Science, University of Basrah, Iraq

Corresponding author: Zaid Noor Obaid Al-Husseini, E-mail: noorzaid297@gmail.com, Mobile: +964 780 425 6657

ABSTRACT

Background : Spectrophotometric procedures are well-liked because of their ease of use, speed, affordability, and wide range of applications. UV spectrophotometry is the most sensitive and precise optical technique for detecting dangerous metals.

Aim of the study: The present study aimed to describe how to measure Aluminum (III) spectrophotometrically quickly and accurately using Alizarin dye in a pharmaceutical sample and aqueous solution

Methodology: The method (mole ratio) was used to determine the stoichiometry of the complex procedures (2:1) (reagent: ion), after which the calibration graph, repeatability, interferences, and applications were examined.

Results: The method is based on the spectrophotometry detection of Alizarin at 494 nm for the determination of Aluminum (III). Besides a detection limit of 0.018 mg/l, the approach enables the determination of a linear range of (0.02-2) mg/l. The relative standard deviation for 1 mg/l is calculated to be 0.6106% with n = 10.

Conclusion: After setting the suitable estimation circumstances (pH, concentration, volume, and concentration of Alizarin Dye, duration, and temperature), Aluminum was evaluated using UV-VIS (III). Stability and stoichiometry of 10-4M Alizarin (2:1). Linearity (0.020-2) mg/l, sensitivity 0.011 mg/cm², reagent limit 0.018 M. (91.670-97.340%) retrieved with the spectral approach for detecting Aluminum (III) in diverse samples

.Keywords: Determination, Spectrophotometric, Alizarin dye, Aluminum (III).

INTRODUCTION

Spectrophotometric methods are widely utilized due to their simplicity, rapidity, low costs also wide applications ^[1]. Among the optical approaches, UV spectrophotometry seems to be the most accepted analytical technique for the determination of hazardous metals, as it delivers sensitive, precise, also accurate measurements of compatible analytes. Moreover, visible spectrophotometric detection is a far more practical technology for the development of portable, online, or at-line systems ^[2].

Alizarin (1,2-dihydroxy-9,10-anthraquinone) Anthraquinone derivatives are kind of the most indicators for low-polar solvents. Analytical reagents in general, Alizarin is also used in chemical analysis. The maximum absorption wavelength of the neutral, non-dissociated form is 430 nm ^[3-8].

Is an unnecessary trace metal ion of widespread distribution. It is the third most prevalent metal ion in the biosphere, accounting for approximately 8% of the earth's surface ^[9] pertaining to the determination of the aluminum by the volumetry method and the detection limit was 9×10^{-8} M and relative standard deviation for the method is found 3.2% ^[10]. To determinate aluminum by the Electrical chemical method and the detection limit was 25 micromoles ^[11]. The purpose of this research is to determine aluminum (III) using the alizarin spectrophotometric technique.

MATERIALS AND METHODS

Balance-sensitive Analytical Instrument of Denver, USA, and a spectrophotometer Shimadzu UV-1700 spectrophotometer, Hitter thermal Ardeas 51, Ismatic,

Homemade valves, 450 μ L flow cell capacity, pH meter, WTW 720.

Chemicals

- 1- Prepared 1000 mg/l of Aluminum ion via dissolving 12.3551g of $[\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}]$ in 1000 mL of distilled water with the addition of 2 mL of H_2SO_4 Concentrated (18), followed by the preparation of additional solutions according to the dilution law.
- 2- Preparation of 0.001 M of Alizarin by dissolving 0.0240 g of Alizarin in 50 mL of pure alcohol, next transferring to a 100-mL volumetric flask and marking with distilled water.
- 3- Preparation of buffering agent pH=6-7 [0.1M Sodium Carbonate + 0.2M hydrochloric acid] that 2.5 g of Sodium Carbonate in filtered water at pH=6-7 [0.1M Sodium Carbonate + 0.2M hydrochloric acid]. 50 mL has transferred to a 250-mL volumetric flask, which was then filled to the sign with filtered water. Set 0.2 M of hydrochloric acid using a dilute, and low-concentration reagent with a specific gravity of 1.8 and a purity of (36-37.5) % after preparing a solution by carbonate solution standardization ^[12].

Statistical Analysis

Data analysis was carried out utilizing IBM-SPSS version 24. The statistical significance was assessed utilizing the Kruskal-Wallis. We used ANOVA for continuous data comparison and the Chi-square test for frequency comparison. If the P-values were less than

0.05, we regarded the findings as statistically substantial.

Ethical Approval

This study approved from the committee and research ethics of Basrah University.

The authors have no conflicts of interest with any individual or organization. There is proof that the present study was done in full accordance with the ethical standards set out in the Declaration of Helsinki in 1964 and its later changes, or with other ethical standards that are similar.

RESULTS

1- Determination of the maximum wavelength:

Using UV visible spectroscopy, the λ maximum wavelength for the reagent and complex has been established, and the optimal conditions for the complex have been determined. As shown in **Figure. 1**, the λ_{max} of the dye was 432nm also the complex Al (III) with Alizarin was 494nm.

Figure. 1: Uv-Vis spectroscopy for Aluminum complex also reagent

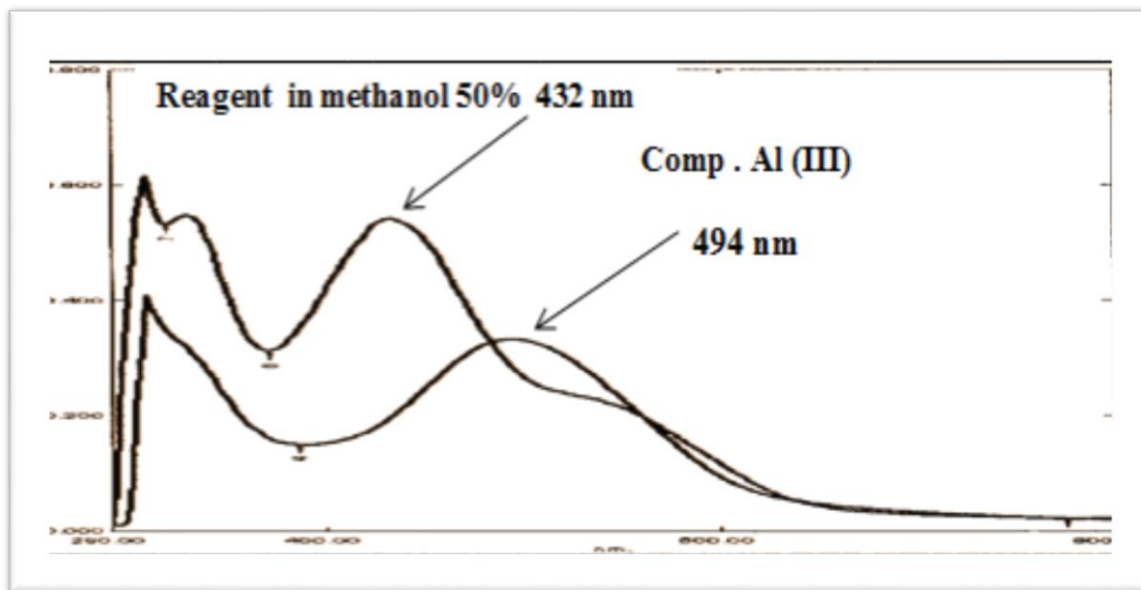


Figure 1: The Effects of pH on Absorption

2- Preparation of the optimal condition of complexation affecting pH value

The optimum pH was [6-7] after preparing a buffer of hydrochloric acid (HCl) and sodium carbonate (Na₂CO₃), as shown in **Table 1** and **Figure 2**.

Table 1: Al (III) con. = 0.1ppm , [Alizarin] =0.001M , volume of ion=2mL,volume of Alizarin=2mL , room temp.

No.	pH	Abs			Average	S.D	R.S.D%
1	3	0.022	0.021	0.021	0.021	0.0007	3.333
2	4	0.023	0.022	0.023	0.023	0.0007	3.043
3	5	0.025	0.025	0.025	0.025	0.000	0.000
4	6	0.027	0.027	0.027	0.027	0.000	0.000
5	7	0.027	0.027	0.028	0.027	0.0007	2.592
6	8	0.024	0.024	0.024	0.024	0.000	0.000

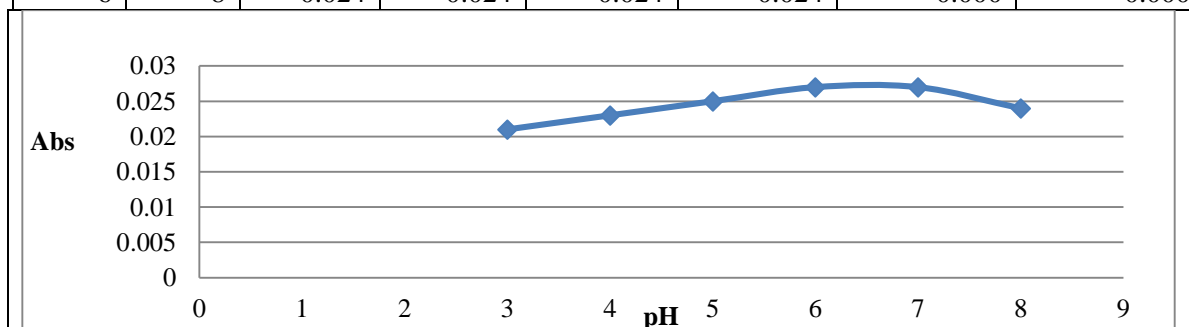


Figure. 2: The influence of pH

3-Determination of the influence of reagent concentration

To increase the peak height, the concentration of the reagent was adjusted between (1×10^{-7} and 1×10^{-3}) M. Chart 2 and Figure 3 illustrate the effect of reagent concentration on Aluminum absorbance (III). Maximum absorption was achieved with 1×10^{-4} M reagent; therefore, 1×10^{-4} M reagent was chosen for future tests. The absorption stability is 10-3 m **Table 2 and Figure 3**

Table 2: Influence of the reagent concentration at the absorption at Al (III) con. = 0.1ppm, volume of ion=2mL, volume of Alizarin=2mL, pH=6-7, room temp

NO.	Alizarin con.(mol/l)	Abs			Average	S.D	R.S.D%
1	1×10^{-7}	0.010	0.011	0.012	0.011	0.001	9.090
2	5×10^{-7}	0.014	0.015	0.015	0.015	0.0007	6.666
3	1×10^{-6}	0.018	0.018	0.019	0.018	0.0007	3.888
4	5×10^{-6}	0.020	0.020	0.020	0.020	0.000	0.000
5	1×10^{-5}	0.022	0.021	0.023	0.022	0.001	4.545
6	5×10^{-5}	0.025	0.025	0.024	0.025	0.0007	2.800
7	1×10^{-4}	0.027	0.027	0.027	0.027	0.000	0.000
8	1×10^{-3}	0.027	0.027	0.027	0.027	0.000	0.000

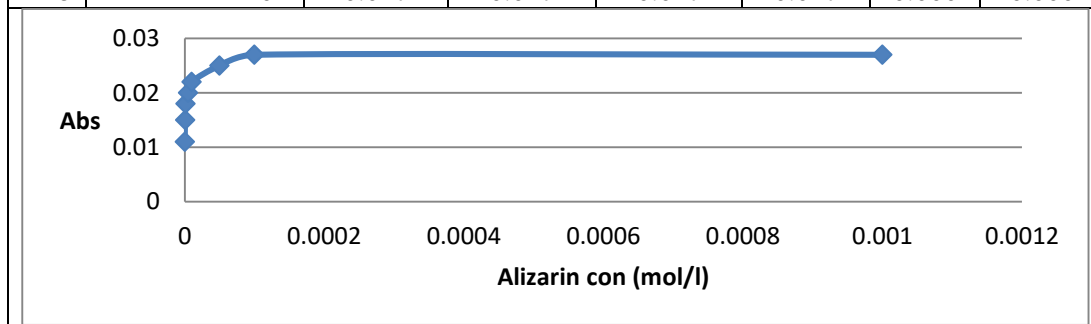


Figure. 3: The influence of reagent concentration

4-Influence of the volume of ion

The complex has made by combining 2 mL from 1×10^{-4} M from the reagent with various volumes of 0.1 mg/l of the metal ion at a pH of 6-7 (**Figure 4 and Table 3**). The optimal complexation volume was 2 mL from the metal ion and 2 mL from the reagent, with a ratio of 1:1.

Table 3: The influence of ion volatilities on absorption at Al (III) con. = 0.1ppm, [Alizarin] =0.001M, volume of Alizarin=2mL, pH=6-7 , room temp

NO.	Volume ion(mL)	Abs			Average	S.D	R.S.D%
1	0.5	0.019	0.020	0.019	0.019	0.0007	3.684
2	1	0.021	0.021	0.021	0.021	0.000	0.000
3	1.5	0.025	0.024	0.024	0.024	0.0007	2.916
4	2	0.027	0.027	0.027	0.027	0.000	0.000
5	2.5	0.020	0.021	0.022	0.021	0.001	4.761

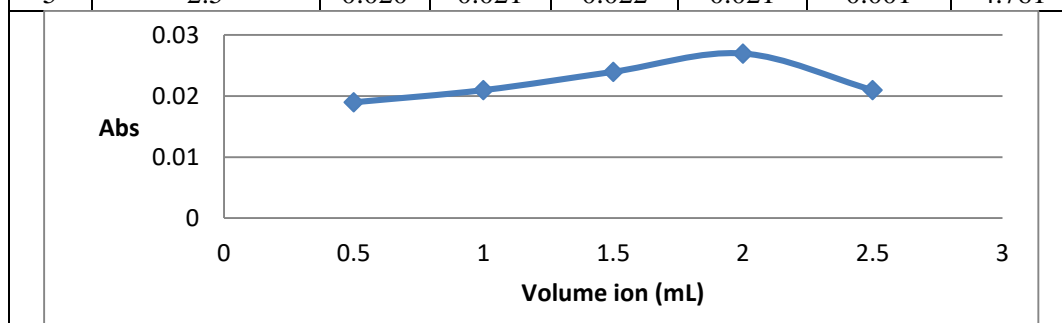


Figure. 4: Influence of metal ion volume

5-Influence of the time

The present research was undertaken to test the stability complex, and it was also determined that the complex was stable for 1440 minutes (Table 4 and Figure 5).

Table 4: Influence of the time on the absorption at:

Al (III) con. = 0.1ppm , [Alizarin] =0.001M , volume of ion=2mL, volume of Alizarin=2mL , pH=6-7 , room temp.

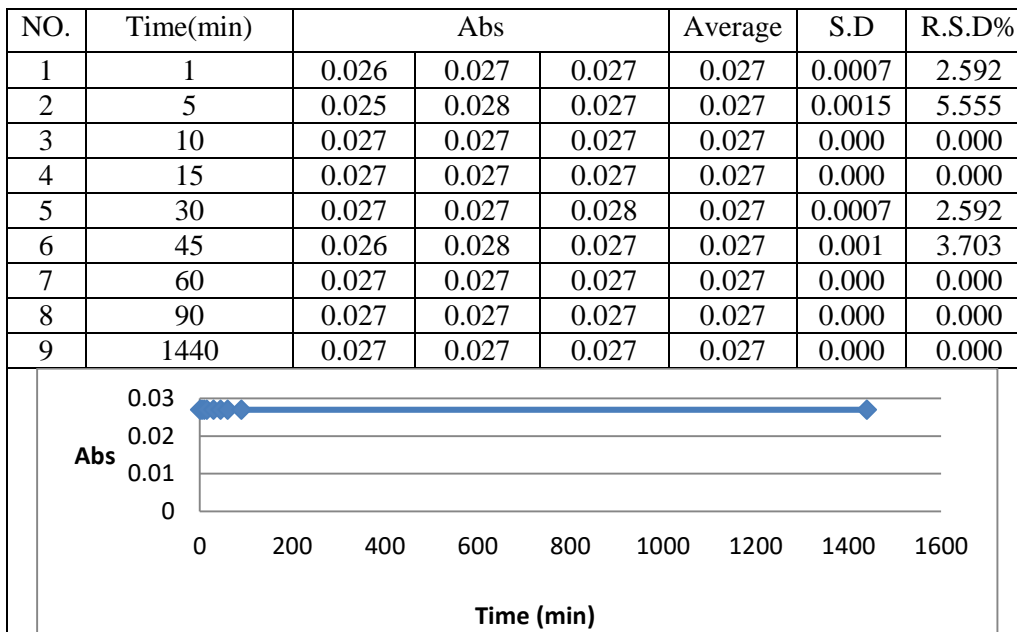


Figure. 5: Stability for complex with time

6- influence of temperature

The Complex was produced at varying temperatures (5–60 °C) (Table 5 and Figure 6).

Table 5: Influence of the time on the absorption at:

Al (III) con. = 0.1ppm , [Alizarin] =0.001M , vol of ion=2mL, volume of Alizarin = 2mL , pH = 6-7 , room temp.

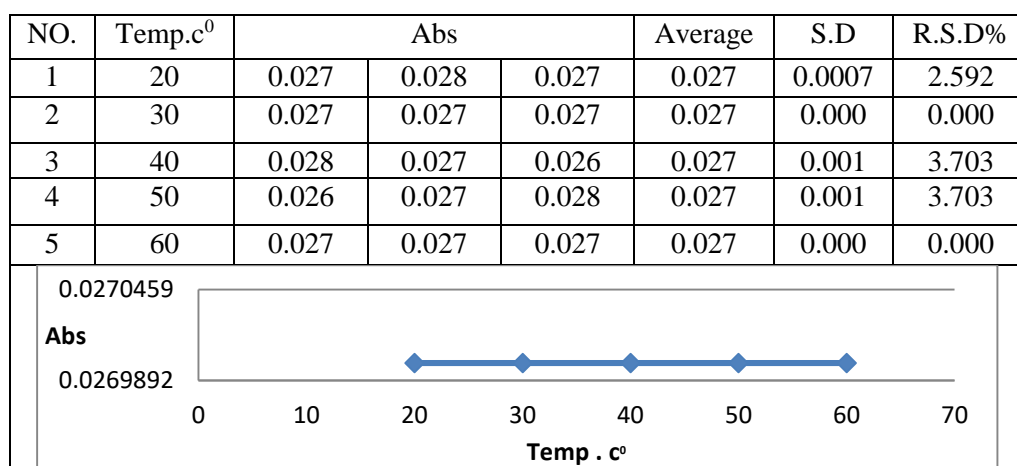


Figure. 6: Stability for complexes with temperature

7-Study influence on stoichiometric production of complex

Using a sophisticated way of mole ratio, equivalents have been examined via the use of a complex approach to mole ratio. The outcome revealed that the complex ratio has 1:1 (Table 6 and Figure 7).

Table 6: mole ratio for Al (III) complex at:
Al (III) con. = $1 \times 10^{-3}M$, [Alizarin] = $1 \times 10^{-3}M$, volume of ion = 2mL, pH = 6-7, room temp.

NO.	No. mol Alizarin / No. mol. ion	Abs			Average	S.D	R.S.D%
1	0.5	0.000	0.000	0.000	0.000	0.000	0.000
2	0.75	0.016	0.015	0.015	0.015	0.0007	4.666
3	1	0.026	0.025	0.027	0.027	0.0015	5.555
4	1.25	0.043	0.043	0.043	0.043	0.000	0.000
5	1.50	0.058	0.058	0.057	0.058	0.0007	1.206
6	1.75	0.068	0.068	0.068	0.068	0.000	0.000
7	2	0.072	0.072	0.074	0.073	0.001	1.369
8	2.125	0.074	0.075	0.075	0.075	0.0007	0.933
9	2.37	0.075	0.075	0.075	0.075	0.000	0.000
10	2.5	0.075	0.075	0.075	0.075	0.000	0.000

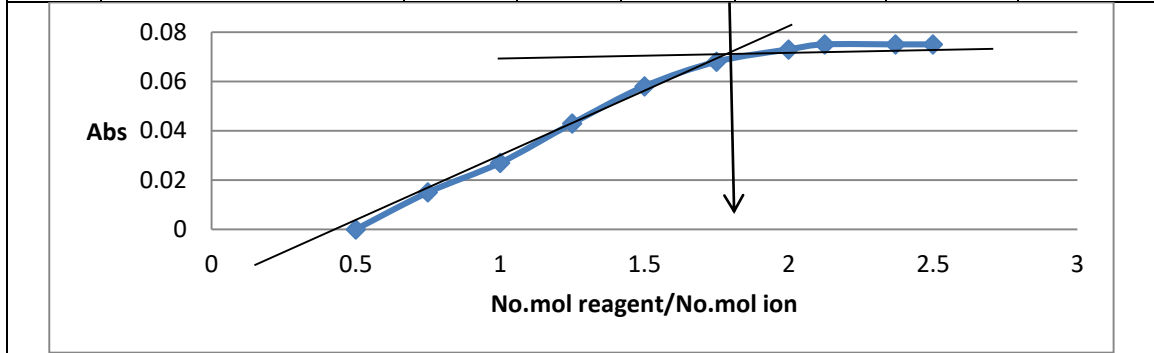


Figure. 7: Mole ratio for complex formation

8-Calibration graph

Calibration graphs were created under optimal complexation and metal ion concentration conditions; the results are shown in **Table 7 and Figure 8**. The calibration graph is linear between 0.02 mg l⁻¹ and 2 mg l⁻¹

NO.	Con. of Al(III) mg/L	Abs			Average	S.D	R.S.D%
1	0.02	0.019	0.018	0.019	0.019	0.0007	3.684
2	0.06	0.025	0.025	0.027	0.026	0.0012	4.615
3	0.1	0.027	0.028	0.029	0.028	0.001	3.571
4	0.15	0.030	0.031	0.031	0.031	0.0007	2.258
5	0.2	0.035	0.035	0.035	0.035	0.000	0.000
6	0.4	0.054	0.054	0.054	0.054	0.000	0.000
7	0.6	0.071	0.071	0.071	0.071	0.000	0.000
8	1	0.131	0.130	0.132	0.131	0.001	0.763
9	1.5	0.167	0.167	0.167	0.167	0.000	0.000
10	2	0.196	0.196	0.195	0.196	0.0007	0.357

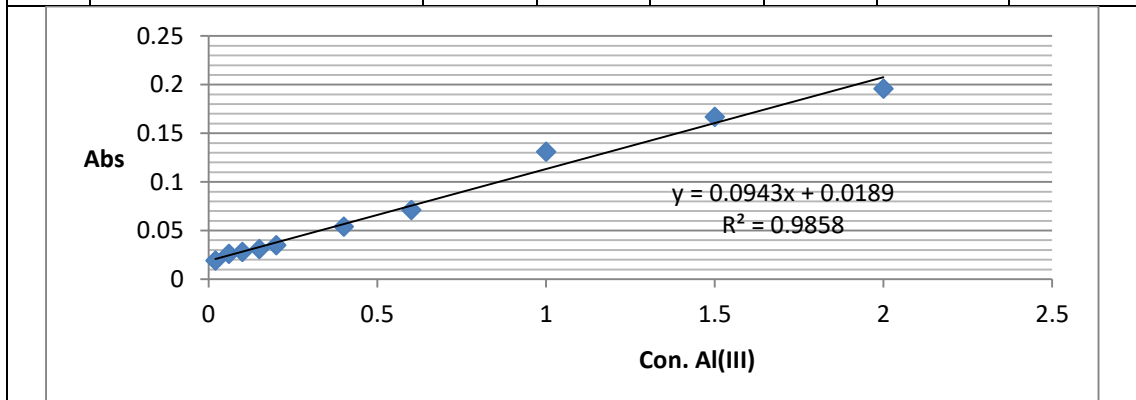


Figure. 8: Calibration graph of Aluminum ion

9-Reproducibility

The results of an experiment designed to determine the accuracy and influence of a system for determining the ion Aluminum (III) by injecting and measuring the substance multiple times at a concentration of 1 mg/L and then comparing the results are shown in **Table 8** and **Figure 9**. The results show that the standard deviation for the 1 mg/L concentration is 0.0008 and that the relative standard deviation is 0.606%.

Table 8: Reproducibility for 1 mg/L of Al (III)

No.	1	2	3	4	5	6	7	8	9	10	Average	S.D	R.S.D%
Abs	0.131	0.131	0.130	0.130	0.131	0.130	0.131	0.132	0.132	0.132	0.131	0.0008	0.6106

Figure. 9: Reproducibility Al (III) for 1 mg/L with Alizarin

The detection limit calculated using the law (D.L. = (3con. S.D.) / Average) was also found to be 0.018 mg/L based on the findings of the reproducibility research.

10-Interference

At a wavelength of 494 nm, where the Average Absorption is studied, the overlap of certain anions also cations, and Aluminum ions in the Aluminum complex forming. the complexity Aluminum was 0.035 when the Aluminum ion concentration in the compound was (0.2 mg/L) the anion and cation (Na⁺, Ca²⁺, Ni²⁺, Pb²⁺, NO₃⁻, K⁺, Mg²⁺, CH₃COO⁻, SO₄²⁻, PO₃³⁻, Cl⁻ are not interference with Aluminum ion:), but Cu¹⁺, Zn²⁺ & Fe³⁺ were intervention with Aluminum ion, the outcome seen in **Table 9**.

Table (9) interference of some cations with complex Aluminum (III)

No.	Ion	Con. mg/L	Average Abs.	Interference	Treatment with suiChart masking
1	Al ⁺³	0.2	0.035	-	-
2	Cu ⁺²	0.1	0.056	0.021	2 drops of 100 ppm concentration of NH ₃
		0.5			
3	Zn ⁺²	0.1	0.071	0.036	2 drops of 100 ppm concentration of NH ₃
		0.5			
4	Fe ⁺³	0.1	0.071	0.036	2 drops of 100 ppm concentration of KH ₂ PO ₄
		0.5			

11-Applications

A spectrophotometric method system for preparing 0.3 mg/L pharmaceutical samples is also available. The aqueous solution determined that the average absorption for the max of the graph is 0.039, which is equal to 0.3 ppm, and it has the same application for the spectrophotometric method, the results of which are shown in **Table 10**.

Table 10: Applications of determinate Al (III) in Pharmaceutical Sample and aqueous solution by.

No.	Sample*	Take value- mg/L	result value- mg/L	Recovery%
1	Ballox plus	0.3	0.292	97.34
2	Arkalox plus	0.3	0.284	94.67
3	Malaous	0.3	0.275	91.67
4	Moxal	0.3	0.283	94.34
5	Aqueous solution	0.3	0.287	95.67

DISCUSSION

UV-VIS was used to estimate the triple aluminum ion, after studying the best conditions for the estimation process. First, the effect of the pH function in the reaction system was studied.

Different values of the pH ranged from (3-8) to use, showing that the pH function was (6-7) It is the best value that corresponds to the highest absorbance [13]. after which a suitable buffer solution was prepared by mixing 29.5 ml of Na₂CO₃ at a concentration of 0.1 M with 20.5 ml of hydrochloric acid at a concentration of 0.2 M to obtain a solution with a pH between (6-7) for use in subsequent experiments Then the effect of the ideal concentration of alizarin dye was studied in the formation of the triple aluminum ion complex Different concentrations of alizarin dye were prepared to study the effect of the ideal concentration.

The ideal concentration of alizarin dye was 1×10^{-4} M. After this concentration, the absorption values were stabilized^[14]. where different solutions of the concentration of the alizarin dye were prepared. Then, the effect of the size of the triangular aluminum ion on the formation of the complex was studied. Different volume ratios of the triangular aluminum ion and a fixed volume of alizarin dye were prepared, and it was found that the best volume ratio was (1:1), or 2 ml of the triangular aluminum ion with 2 ml of the triangular aluminum ion[15].

The stability of the complex was studied for 1 minute to 1440 minutes, as it was found that the complex is stable during all these periods with a constant absorbance. And I studied the effect of the temperature difference on the stability of the triple aluminum ion complex. The complex was prepared at different temperatures ranging between (20-60) °C.

It was found that the complex is stable during this range. The study was conducted under the best conditions that had been determined in previous experiments, and it happened at a temperature of 60 °C, it happened. An increase in the absorption values is due to the effect of temperature on the concentration of the solution, which led to this increase as a result of the evaporation of the solvent. Then, the valence of the aluminum ternary complex was studied using the molar ratio method, as it became clear that the molar ratio of the alizarin dye and the ternary aluminum ion are (1:2)[13].

The range of linearity was between (2 and 0.020) mg/l when we obtained a calibration curve, and Sandel's sensitivity to the method, depending on the results of the calibration curve, was 0.011 µg/cm².

Then study the extent of accuracy and efficiency of the method used in estimating the triple aluminum ion by repeating the process of measuring the absorption several times using a concentration of 1 mg/liter, as it becomes clear how accurate the results are, as the value of the standard deviation was 0.0008 and the value of the relative standard deviation was

0.6106% [16], which indicates the accuracy and efficiency of the method used In the estimation of the triple aluminum ion and through an iterative study, the detection limit was calculated and found to be 0.018 mg/l according to the law $D.L = 3 \times S.D \times Con. \div Mean$ Then several interactions between negative and positive ions were studied to find out their effect on the process of estimating the tri-aluminum ion.

As for the ions that interfered with the tri-aluminum ion, they were treated with a suitable mask [17,18]. Different samples of drugs were taken that contain small amounts of the tri-aluminum ion and were estimated using alizarin dye.

REFERENCES

1. **Filik H, Tutem E, Apak R, Erc E (1998):** Spectrophotometric determination of aluminum and indium with 2,2',3,4-tetrahydroxy-3',5'-disulphoazobenzene. *Microchim. Acta.*, 129: 57-63.
2. **Suresha S, Silwadi M, Syed A (2002):** Sensitive and Selective Spectrophotometric Determination of Hg(II), Ni(II), Cu(II) and Co(II) Using Iminodibenzyl and 3-Chloroiminodibenzyl as New Reagents and Their Applications to Industrial Effluents and Soil Samples. *International Journal of Environmental Analytical Chemistry*, 82 (5): 275-289.
3. **Ezati p, Rhim J (2020):** pH-responsive chitosan-based film incorporated with alizarin for intelligent packaging applications. **DOI: 10.1016/j.foodhyd.2019.**
4. **Hosseini M, Asadi M (2009):** new design of flow injection unit for determination aluminum (iii) by alizarin dye. *International Journal of Current Research in Chemistry and Pharmaceutical Sciences*, 25:807-812.
5. **Cysewski P, Jelinski T, Przybylek M, Shyichuk A (2012):** Color prediction from first principle quantum chemistry computations: a case of alizarin dissolved in methanol. *New Journal of Chemistry*, 36: 1836-1843.
6. **Chamsaz M, Zavar M, Hosseini M (2000):** Flotation spectrophotometric determination of aluminum with alizarin. *Anal Lett.*, 33:1625-1633.
7. **Feng G, Jiang L, Liu D, Chen C (2011):** Interaction between Alizarin and Human Serum Albumin by Fluorescence Spectroscopy. *ANAL. SCI.*, 27:79-84.
8. **Say-Liang-Fat S, Cornard J (2011):** Al(III) complexation by alizarin studied by electronic spectroscopy and quantum chemical calculations. *Polyhedron*, 30:2326-2332.
9. **Burtis C, Ashwood E, Tietz N (1999):** Text Book of Clinical Chemistry. 3rd Edi. Philadelphia: W.B. Saunders Company. Pp.984-986.
10. **Tang Y, Sun C, Yang X, Shen R (2013):** Graphene Modified Glassy Carbon Electrode for Determination of Trace Aluminium(III) in Biological Samples. *International Journal of Electrochemical Science*, 8(3): 4194 - 4205.
11. **Seung-Cheol, C (2010):** Alizarin Red S modified electrochemical sensors for the detection of aluminum ion. *Journal of Sensor Science and Technology*, 19(6): 421- 427.
12. **Owadh H, Hameed S (1984):** Principle of Analysis Chemistry, Foundation Technical Institutes, Ministry of

Higher Education and Scientific Research, Pp. 165. (Arabic edition).

13. **Sathish R, Kumar M, Rao G, Kumar K and Janardhana C (2007):** Optical Sensing of Fluoride Through a Self-Organized Fluorescent Ensemble of Quinizarin-Al(III) Complex, *Spectrochim. Acta, Part A.*, 66: 457– 461.
14. **Yariv S, Epstein M (2003):** Visible-spectroscopy study of the adsorption of alizarine by Al-montmorillonite in aqueous suspensions and solid state *J. Colloid Interface Sci.*, 263: 377–385.
15. **Yew P, Lee Y (2010):** Quantitative determination of Al(III) ion by using Alizarin Red S including its microspheres optical sensing material. *Sensors*, 10: 9963– 9981.
16. **Safavi A, Bagheri M (2005):** A novel optical sensor for uranium determination *Anal. Chim. Acta.*, 530: 55– 60.
17. **Chen Z, Wang Z, Chen J and Chen X (2012):** Alizarin red S/copper ion-based ensemble for fluorescence turn-on detection of glutathione with tunable dynamic range *Biosens. Bioelectron.*, 38:202– 208.
18. **Musa A, Narayanaswamy R (1995):** Development of an optical fiber Al(III) sensor based on immobilized chrome azurol S *Talanta*, 42: 1337– 1344.