New flow Injection System Compared with Direct Spectrophotometric for Determination Al (III) in Pharmaceutical Samples

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Abstract
A new flow injection merging zone system was designed for the determination of Aluminum (III) using the Alizarin red S (ARS) reagent and compared with the spectroscopic method. The complex formation at the wavelength of maximum absorption of 481 nm in two simple methods for the determination of Aluminum (III) where the calibration curves were linear over the concentration ranges of (0.03 – 10) and (0.08 – 10) µg. ml-1 for both the spectroscopic method and the flow injection method, respectively, as well as the detection limits (LOD) and the limits of quantities (LOQ) (0.26, 0.088), (0.29, 0.097) µg. ml-1, respectively, and the effects of various experimental factors and the amount of Aluminum (III) in pharmaceutical formulations were studied.
Key words: Aluminum (III), Merging Zone, Determination, Alizarin Red S

1. Introduction

Aluminum is an element of the third group of metallic elements in nature. It is the most abundant of all metal cations. It shows ionic and covalent bonding. It was discovered in the nineteenth century and became an important part of everyday life [1]. Aluminum is characterized by a high ratio of strength to weight, good thermal conductivity, and corrosion resistance. It is a recyclable metal and is important in various industries [2,3]. There is increasing concern about the high concentrations of Aluminum in the environment because it is insoluble at a high rate. The interactions that take place between foodstuffs and packaging materials can be a source for the release of Aluminum that enters the human body, as well as through medicines and the environment [4,5,6].
Aluminum is not pure in nature, but it is related to other elements such as feldspar, alum, and bauxite. Aluminum alloys are preferred because they have a set of properties and are widely available on the market [7,8,9,10,11,12]. Long exposure to Aluminum leads to Alzheimer's disease, and it was also found that the concentration of Aluminum is higher in some bone samples than in patients with kidney failure, and neurological diseases were found to be due to high levels of Aluminum in the brain [13, 14,15,16].
Alizarin red S (ARS) was used to interact with cu_2 in the spectroscopic determination of cysteine in pharmaceutical products [17]. Alizarin red S was used in the technique of stripping anodic pulse voltmeter [18] . Alizarin red S has been used as a natural dye in dyed fabrics [19] . Also, Alizarin red S dye and normal light microscopy were used to detect microcrystalline or amorphous Calcium phosphate salts in a quick and simple assay [20] . While the use of Alizarin red with Alcian Blue in the evaluation of skeletal growth in the fetus of rodents [21]. Different analytical methods have been notified for the determination of Aluminum such as: reverse flow injection (rFIA) at λmax (468nm), Ph (5.4) ,and LOD(1.9)µg.L^{-1} [22] . injection flow [FIA] LOD (5) µg. L^{-1}[23]. Spectrophotometric at λmax (623nm) and LOD (0.001) µg. L^{-1}[24]. Indirect atomic absorption LOD (95) µg. L^{-1}[25]. liquid liquid extract LOD (0.25) µg. L^{-1}[26].
The aim of this study was to develop a spectrophotometric flow injection technique for measuring Al (III) in pharmaceutical samples that was rapid, accurate, and selective.

2. 2. Experimental

2.1. Apparatus

All absorption measurements were performed with a Biochrom Libra S60 dual-beam spectrophotometer, an Oakton 2100 mV/Ion/C/F Oakton series pH meter, and an Oakton 2100 mV/Ion/C/F Ohans PA214 series pH meter. Tubes were used as the material. Figure 1 depicts the flow injection system utilized for aluminum dertermine, which included an ismatec peristaltic pump to push the carrier stream solution, and the sample and reagent solutions were loaded and injected through a laboratory produced valve (consisting of four secondary valves each with three outlets), an (OPTIMA SP300) UV-Visible detector was employed, and a C1032 Hilter Ardeas 51 recorder was used to record the signal pen.

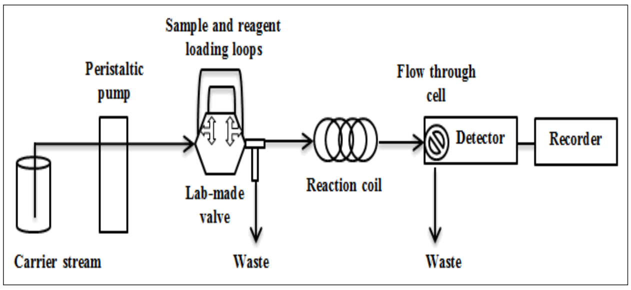

Figure1: Schematic diagram of FIA manifold for the determination of Al (III)

2.2. Chemicals and reagent

All of the chemicals used were analytical reagent grade, with aluminum sulfate (99% purity) supplied from Merck Chemical Company and alizarin red S (99% purity) obtained from Fluka.

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2.3. Preparation of Solutions

A stock solution (100 mg. L-1) of aluminum sulfate was prepared by dissolving 0.0634 g of aluminum sulfate in 100 mL of distilled water, then the working solution was diluted further. A stock solution of (1 × 10-3 N) of Alizarin red S (ARS) was prepared by dissolving 0.3422 g in 100 ml of Buffer solution in spectral method, and it was dissolved with 100 ml of distilled water in flow injection method and a buffer solution(0.1 N acetic acid with Sodium acetate 0.1 N)

Maximum absorption wavelength Determination

The spectra of Al (III) and the ARS reagent were obtained against their blank solutions as shown in Fig. 2, which gave a maximum absorption at 481 nm for complex and 425 nm for the ARS reagent.

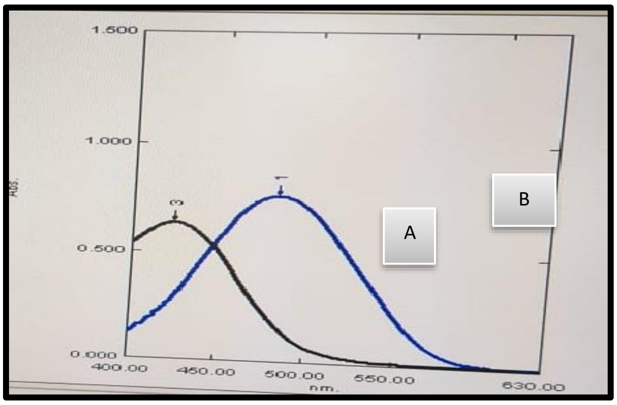

Fig 2: UV-Vis spectrum for Aluminum (III) and reagent in pH= 5, A: of ARS, B; of complex for Al(III).

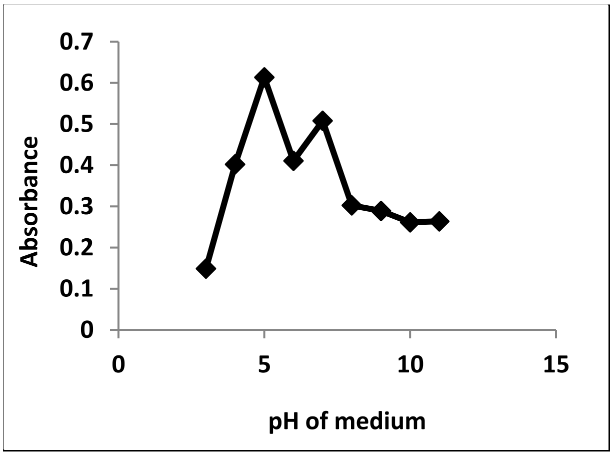

Fig.3: The effect of the acidity function

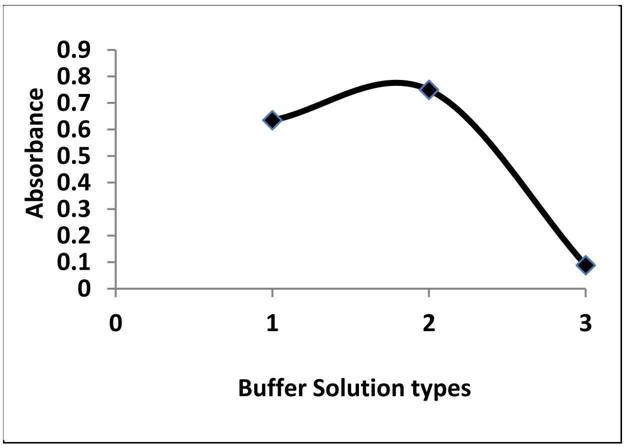

Fig.4: The effect of buffer solution, 1: without buffer, 2: acetate buffer ,3: citric buffer

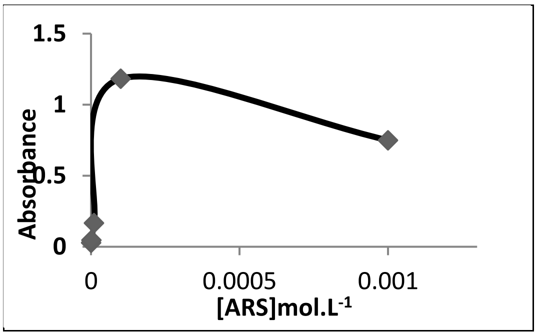

Fig.5: The effect of the Concentration of ARS

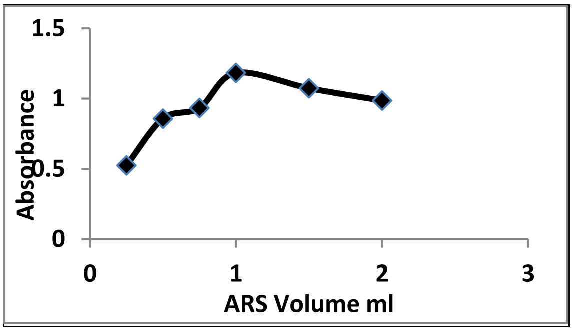

Fig.6: The effect of the volume of ARS

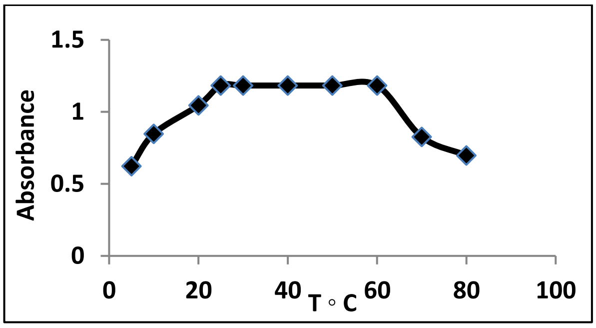

Fig.7: The effect of the Temperature

3. Results and Discussion

Experimental variables effect

Spectral method

The first variable investigated was the best pH in which the reaction take place. this parameter was tested in the range of 3-11. As can be seen in Fig.1 maximum absorbance signals was at pH equal 5. The type of buffer solution (1: with out buffer solution, 2: acetate and 3: citric buffer solution) the result shown in Fig.2 and acetate buffer was give highest absorbance.

The influence of the concentration of ARS reagent on the analytical signal was examined therefore ARS solution in the concentration range of (1×10-7 – 1×10-3) mol. L-1were tested and maximum signal were observed for (1×10-4)mol.L-1 ,Fig.3 . the effect of reagent volume investigated, it was tested in the range of 0.1-2 ml, 1ml give the best result as shown Fig.4. the temperature of the reaction was study in the range of 5- 80 °C, the result shown in Fig.5, and it turns out through the results that the reaction stable among 15-30°C.

Flow injection method [27]

The first variable investigated was the best pH at which the reaction takes place. As shown in Fig.8, the maximum absorption signals occur when the pH is equal to 5. Injection flows the result is shown in Fig. 9 and the injection flow of 4.1 ml.min-1 gives the highest absorption. The effect of the length of the reaction coil was examined, as this parameter was tested in the range of (10–30) cm, and 20 cm gave the highest absorption in Fig.10, The effect of ARS reagent concentration on the analytical signal was examined, so the ARS solution was tested in a concentration range of (1×10-3 - 1×10-7) mol.ml-1, where the maximum signal was tested and observed (1×10-4) mol.ml-1. Fig.11, The effect of the reagent volume was tested in the range of (39.25–157) μL. 117.75 μL gives the best result as shown in Fig.12, The effect of ion size was tested in the range of (39.25–235. 5) μL, 157 μL gives the best result as shown in Fig.13.

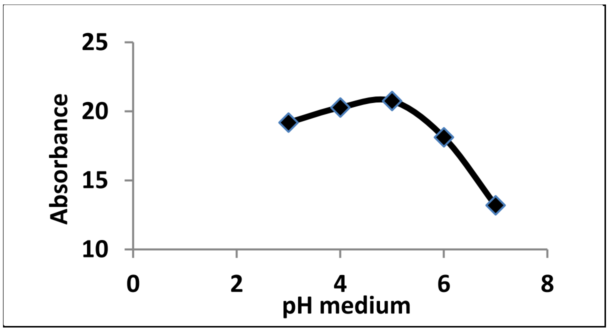

Fig 8: pH medium influence on complex formation

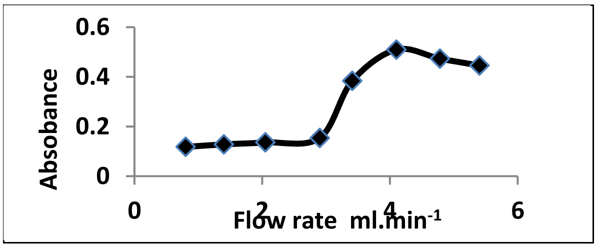

Fig 9: Flow rate influence on complex formation

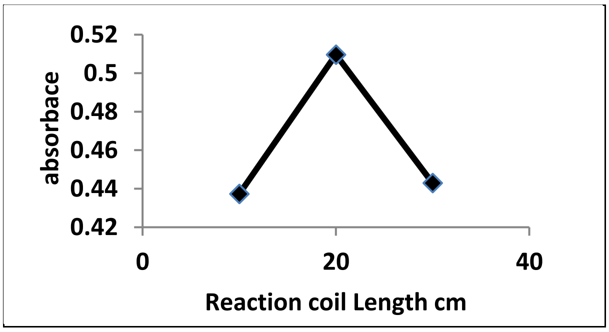

Fig 10: The reaction coil length influence on complex formation

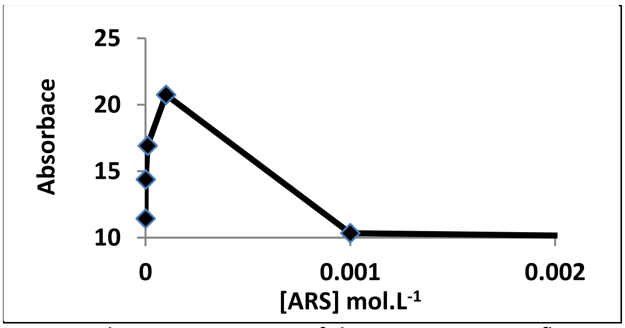

Fig 11: The concentration of the ARS reagent influence on complex formation

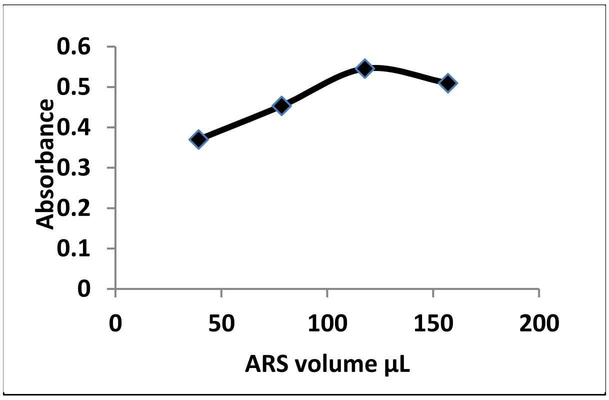

Fig 12: ARS volume influence on complex formation

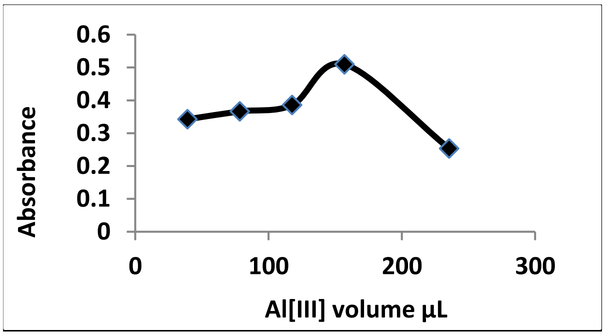

Fig 13: Sample volume influence on complex formation

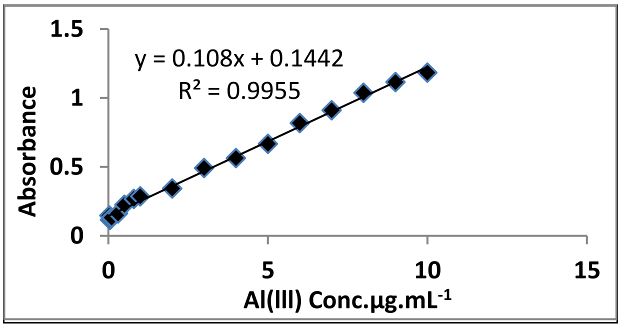

Figure 14: Calibration curves of Al (III) in spectral method

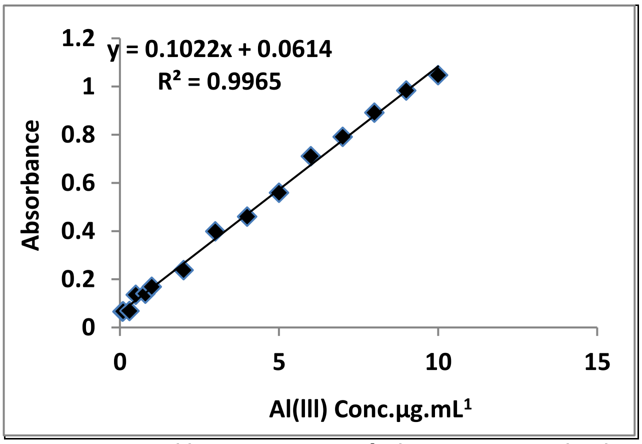

Figure 15: Calibration curves of Al (III) in FIA method

Calibration curves in two methods

Under optimal conditions, Al(III) was determined and calibrated curve at 481 nm were prepared .The two proposed methods spectral and flow injection were obey of Lambart – Beer Law at range (0.03 – 10.0) and (0.08 – 0.10) μg ml^{-1}, respectively . The limits of quantities and limits of detection were (0.088, 0.26) , (0.097, 0.29) μg ml^{-1}, respectively as shown in Figure 14 and 15

Effect of Interference

To know the effect of ionic interference on the height of the absorption peak at wavelength 481 nm and how to treat it if any interference or effect is found (Cu2+, Zn2+, Ni2+, Mg2+, Mn2+, Cl-, CO32+, PO43-, CH3COO-, SO42 -). The study discovered that the aforementioned ions have no effect on the Al (III) ion when it forms a complex with ARS using the flow injection method. In addition, small changes in the height of the absorption signal are treated by an appropriate masking factor according to the spectroscopic method, as shown in Table 1.

Table 1: The effect of ion interference in the Al (III) compound according to the spectroscopic method

Interference Iones	Conc. Interferences µg.mL-1	Conc. AL3+ µg.mL-1	The change in Absorbance	Treatment with suitable masking
Without Interferences		10	1.183	
Fe 3+	10	10	-0.498	0.5 mL PO4
	50	10	-0.428	1 mL PO4
Cu 2+	10	10	-0.641	24 drops NaOH
	50	10	-0.307	24 drops NaOH
Zn 2+	10	10	-1.110	5 drops NH3
	50	10	-1.087	5 drops NH3
Mn 2+	10	10	-1.052	24 drops NaOH
	50	10	-1.060	25 drops NaOH

Applications

The proposed procedure was successfully used to select Al (III) in pharmaceutical samples according to the two proposed methods. It is evident from Table 2 and 3 that the recovery ratio values range between (96.429–115.714) % and (83.366–104.305) % according to the spectral method and the flow injection method, respectively, which indicates the accuracy of the results and the accuracy of the analytical method used to determine the Al (III) ion within this study

Table 2: Al(III) determination in different pharmaceutical samples in Spectral and FIA methods

FIA method		Spectral method		Taken value µg.ml−1	Pharmaceutical sample, Al conc. in drugs
Recovery%*	Found value µg.ml−1	Recovery%*	Found value µg.ml−1		
104.305	10.4	101.190	10.119	10	Maloox plus. syrup 3.5 mg / 100ml Sonfi-Aventis S.P.A
99.022	9.92	99.048	9.904	10	Proolax 225mg/ 5ml Tabuk pharmaceutical manufacturing co
87.730	8.8	96.429	9.642	10	Acilox plus. 200mg / 1 tab Pioneer
91.116	11.5	105.714	10.571	10	Maloox plus 200mg / 1 tab Sonfi-Aventis S.P.A
91.194	9.12	115.000	11.500	10	Acilox plus . syrup 225 mg/ 5ml Pioneer
83.480	8.32	98.572	9.857	10	Maloox-MDI 225 mg/ 5 ml Modern Company
87.672	8.8	99.762	9.976	10	Moxal plus 215mg/ 5ml Julphar Life
88.768	8.88	115.714	11.571	10	Epicogel 8.1g/ 100ml E.I.P.I.CO.
83.366	8.32	113.809	11.380	10	Antacid 200mg / 1 tab Jedco
89.687	8.96	115.000	11.500	10	Alugel 225 mg/ 5 ml Lincoln
*Average of three times					

Table 1: the analytical parameters of the two proposed methods

Parameter	Spectroscopy method.	FIA method
Wavelength λmax / nm	481	481
pH	5	5
Concentration range / µg ml ^{1}	0.03 - 10	0.08 - 10
Regression equation Y = bx +a	Y = 0.108x + 0.1442	Y= 0.1022x + 0.0614
Slope b	0.108	0.1022
Intercept a	0.1442	0.0614
Correlation coefficient r^2	0.995	0.996
Limit of detection / µg ml ^{1}	0.26	0.29
Limit of quantitation / µg ml ^{1}	0.088	0.097
Volume of ion	2 ml	157µl
Volume of ARS	1 ml	117.75µl
Sampling frequency	25 $S.h^{-1}$	90 $S.h^{-1}$
Cost	high	low
RSD % n = 10	0.314	0.171
Molar absorption coefficient ε L mol^{-1} cm^{-1}	2.914×10^{3}	2.759×10^{3}
Sandell's sensitivity S / µg cm ^{2}	9.259×10^{-3}	9.784×10^{-3}
Recovery %	96.429 - 105.714	83.480 - 104.305

4. Conclusion

Novel injection designs based on merging-zone technology with spectroscopic detection have been successfully established for the determination of Al(III) by reaction with ARS in both pure and pharmaceutical formulations .The laboratory valve, which is a major component of the suggested system, is simple, affordable, and efficient, and is easy to clean, replace, and repair using inexpensive components

References

1- Becaria, A., Campbell, A., and Bondy, S. C. (2002). Aluminum as a toxicant. Toxicology and Industrial Health, 18(7), 309-320.
2- Ashkenazi, D. (2019). How aluminum changed the world: A metallurgical revolution through technological and cultural perspectives. Technological Forecasting and Social Change, 143, 101-113.
3- Chen, Z., Huang, C., Wu, B., Zhao, M., and Yan, W. (2010). Discovery of native aluminum and its possible origin from prospective gas hydrate areas in the South China Sea. Science China Earth Sciences, 53(3), 335-344.
4- Khanhuathon, Y., Siriangkhawut, W., Chantiratikul, P., and Grudpan, K. (2015). Spectrophotometric method for determination of aluminium content in water and beverage samples employing flow-batch sequential injection system. Journal of Food Composition and Analysis, 41, 45-53
5- Rana, R. S., Purohit, R., and Das, S. (2012). Reviews on the influences of alloying elements on the microstructure and mechanical properties of aluminum alloys and aluminum alloy composites. International Journal of Scientific and research publications, 2(6), 1-7.
6- Joshi, S. P., Toma, R. B., Medora, N., and O'Connor, K. (2003). Detection of aluminium residue in sauces packaged in aluminium pouches. Food Chemistry, 83(3), 383-386.
7- Runge, J. M. (2018). A Brief History of Aluminum and Its Alloys. In The Metallurgy of Anodizing Aluminum (pp. 1-63). Springer, Cham.
8- J.R. Davis " Alloying" p351-416 DOI:10.1361/autb2001p351
9- Velmanirajan, K., & Anuradha, K. (2019). Aluminium and Its Interlinking Properties. In Aluminium Alloys and Composites. IntechOpen.
10- Georgantzia, E., Gkantou, M., & Kamaris, G. S. (2021). Aluminium alloys as structural material: A review of research. Engineering Structures, 227, 111372.
11- Saevarsdottir, G., Kvande, H., and Welch, B. J. (2020). Aluminum production in the times of climate change: The global challenge to reduce the carbon footprint and prevent carbon leakage. JOM, 72(1), 296-308.
12- Bolt, A., Dincer, I., and Agelin-Chaab, M. (2020). Experimental study of hydrogen production process with aluminum and water. International Journal of Hydrogen Energy, 45(28), 14232-14244.
13- Antunes, G. A., dos Santos, H. S., da Silva, Y. P., Silva, M. M., Piatnicki, C. M., and Samios, D. (2017). Determination of iron, copper, zinc, aluminum, and chromium in biodiesel by flame atomic absorption spectrometry using a microemulsion preparation method. Energy & Fuels, 31(3), 2944-2950.
14- Ogunlade, B., Adelakun, S. A., and Agie, J. A. (2020). Nutritional supplementation of gallic acid ameliorates Alzheimer-type hippocampal neurodegeneration and cognitive impairment induced by aluminum chloride exposure in adult Wistar rats. Drug and chemical toxicology, 1-12.
15- Nanda, B. B., Biswal, R. R., Acharya, R., Rao, J. S. B., and Pujari, P. K. (2014). Determination of aluminium contents in selected food samples by instrumental neutron activation analysis. Journal of Radioanalytical and Nuclear Chemistry, 302(3), 1471-1474.
16- Nayak, P. (2002). Aluminum: impacts and disease. Environmental research, 89(2), 101-115.
17- Pazalja, M., and Salihović, M. (2021, April). Spectrophotometric Determination of Cysteine Based on Complex Reaction Alizarin Red with Cooper. In International Conference on Medical and Biological Engineering (pp. 474-480). Springer, Cham.
18- Rojas-Romo, C., Aliaga, M. E., Arancibia, V., and Gomez, M. (2020). Determination of Pb (II) and Cd (II) via anodic stripping voltammetry using an in-situ bismuth film electrode. Increasing the sensitivity of the method by the presence of Alizarin Red S. Microchemical Journal, 159, 105373.
19- Jiang, H. Y., Hu, X. D., Zhu, J. J., Wan, J., and Yao, J. B. (2021). Studies on the photofading of alizarin, the main component of madder. Dyes and Pigments, 185, 108940.
20- Paul, H., Reginato, A. J., and Ralph Schumacher, H. (1983). Alizarin red S staining as a screening test to detect calcium compounds in synovial fluid. Arthritis and Rheumatism: Official Journal of the American College of Rheumatology, 26(2), 191-200.
21- Young, A. D., Phipps, D. E., and Astroff, A. B. (2000). Large-scale double-staining of rat fetal skeletons using Alizarin Red S and Alcian Blue. Teratology, 61(4), 273-276.
22- Albendın, G., Manuel-Vez, M. P., Moreno, C., and Garcıa-Vargas, M. (2003). Reverse flow-injection manifold for spectrofluorimetric determination of aluminum in drinking water. Talanta, 60(2-3), 425-431.
23-Røyset, O. (1985). Comparison of four chromogenic reagents for the flow-injection determination of aluminum in water. Analytica chimica acta, 178, 223-230..
24- Wyganowski, C., Motomizu, S., and Toei, K. (1982). Spectrophotometric determination of aluminum in river water with bromopyrogallol red and n-tetradecyltrimethylammonium bromide by flow injection analysis. Analytica Chimica Acta, 140(1), 313-317.

25- Allain, P., Mauras, Y., Beaudeau, G., and Hingouet, P. (1986). Indirect micro-scale method for the determination of desferrioxamine and its aluminium and iron chelated forms in biological samples by atomic absorption spectrometry with electrothermal atomisation. Analyst, 111(5), 531-533.
26- Zhang, J., Xu, H., and Ren, J. L. (2000). Fluorimetric determination of dissolved aluminium in natural waters after liquid–liquid extraction into n-hexanol. Analytica Chimica Acta, 405(1-2), 31-42.
27- Du, Y. J., Yan, J. L., Ni, M., and Du, B. A. (2011). Determination of mercury (II) by spectrophotometric method based on self assembly of gold nanoparticles. Journal of the Iranian Chemical Research, 4(2), 87-91.