

# Design of a Novel Microfluidic Chip for Measuring Aluminum (III) with Alizarin Red S as A Reagent

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## Abstract

The research included the design of a microfluidic chip with two channels, one of which is 7 cm long and the other 6 cm, to be used for determination using the microfluidic injection system. It's a new, simple, sensitive, fast, and inexpensive method. The process depends on the reaction of Aluminum (III) with Alizarin Red S (ARS), spectrographically recorded at 481 nm. The calibration curve, dispersion coefficient, repeatability, interferences, and applications were studied where the linearity ranged between (1.0 - 10.0)  $\mu\text{g mL}^{-1}$ , the detection limits (LOD) 0.03  $\mu\text{g.mL}^{-1}$ , the limits of quantities (LOQ) 0.120  $\mu\text{g.mL}^{-1}$ , and the recovery % were recorded (120.727 – 100.363 %).

**Keywords:** Aluminum (III), Determination, Microfluidic chip, Alizarin Red S. 1.

## 1. Introduction

Aluminum is an important element in human life because of its vital role and many applications and uses [1, 2], and. Most of the Aluminum research is important because it is used in all kinds of industries where aluminum foil is used to coat the electrodes [3-6]. Aluminum alloy is used in the manufacture of car pistons and is also used in the construction of hydroelectric dams [7] and [8]. Since ancient times, Alizarin red (ARS) dye has been used in the textile industry. They are insoluble or poorly soluble in water [9] and [10].

In 1984, Ruzicka described a new approach to the microfluidic system known as the microfluidic system [3, 11] and [12]. Microfluidic wafers containing micro-channels are a platform for biological, chemical, and medical applications, and flow injection into the microfluidic system is progressing significantly today [13] and [14].

The element Aluminum was also estimated in several different ways, such as neutron activation analysis [15]. atomic absorption spectrometry with flame (FAAS) or electrothermal (ETAAS) atomizers [16] and [17]. liquid-liquid extraction (LLE) [18], solid-phase extraction [19]. Quantitative determination [20].

**Table 1. Comparison with other procedures for the extraction of Al(III).**

Method	Reagent	Sample Volume (mL)	Linearity ( $\mu\text{g L}^{-1}$ )	LOD ( $\mu\text{g L}^{-1}$ )	RSD (%)	Refs.
Spectrofluorimetry	8-hydroxyquinoline/Triton X-114	25.0	2.0-200.0	0.79	2.7	(Hakmelahi et al,2017)
rFIA	Salicylaldehyde picolinoylhydrazone	10.0	3-30	0.59	1.98	(Albendin et al,2003)
Spectrophotometry	Chrome Azurol S/cetyltrimethylammonium bromide/Triton X-114	10.0	3.0-100.0	0.52	1.7	(Bahram et al,2007)
FAAS	2-(3- indolyl) - 4,5 di phynyl imidazole/ Triton X-114	15.0	0.2-0.0	13.0	1.3	(Şatiroğlu et al,2010)
SIA	N-heptane	50.0	7.7-120	2.3	1.5	(- Burguera et al,2005)
FAAS	Xylidyl Blue/ Triton X-114	50.0	5.0-800.0	1.43	2.5	(Ulusoy et al,2011)
Stopped-Flow	1-hexylpyridinium	25.0	15-0.06	0.05	1.7	(Abdolmohammad et al,2010)
FAAS	ErioChrome Cyanine-R/Triton X-114	10.0	100-6000	60.0	2.8	(Şatiroğlu et al,2010)
Microfluidic Flow injection	Alizarin red (ARS)	10.0	1.0-10.0	0.03	0.239	This work

In this paper, a valve was designed from available and cheap materials, as it consumes low volumes of ions and small volumes of the reagent, as well as the number of samples measured per s.h-1 is large, there is no interference with foreign ions, and the recovery is large.

The aim of the study is to find a new, simple, low cost, low volume, sensitive and selective method for the determination of Aluminum (III) using  $\mu\text{FIA}$ .

## 2. Experimental

### 2.1. Apparatus

All pH measurements were made using the Oakton 2100 Series pH/mV/Ion/°C/°F Meter, absorbance measurements were made using the Biochrom Libra S60 double beam spectrophotometer, and weighing the samples was performed using the Ohaus PA214 Pioneer Analytical Balance. The flow cell used is 450  $\mu\text{L}$ , Teflon pipes were used to load materials. A peristaltic pump Ismatic was used to push the solutions. The recorder was also used to record the signal Pen Siemens C1032 Hitter

Ardeas 51, The resulting peak was obtained by using a UV-Visible detector (OPTIMA SP300).

### 2.2. Chemicals and reagent

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

### 2.3. Preparation of Solutions

A stock solution (100 mg/L) of aluminum sulfate was prepared by dissolving 0.0634 g of aluminum sulfate in 100 mL of distilled water, and then the working solution was diluted again. A stock solution ( $1 \times 10^{-3}$  N) of Alizarin Red S (ARS) was prepared by dissolving 0.3422 g in 100 ml of distilled water and buffer (0.1 N acetic acid with 0.1 N sodium acetate).

### 2.4. General Procedure

#### 2.4.1. Designing of micro valve

The novel microfluidic chip is composed of low-cost materials readily accessible on the local market and is intended for great efficiency [21].

Figure 1.2 shows a new FIA design and a new microfluidic slide in detail. A microfluidic slide with two 7 cm and 6 cm long channels with (id 0.5 mm) and a 20 cm reaction coil for mixing fluids in a mixing coil, with the ionic solution and reagent channels incorporated into the microfluidic slide. Loading and injection control can be handled by three-way auxiliary valves positioned off the slide.

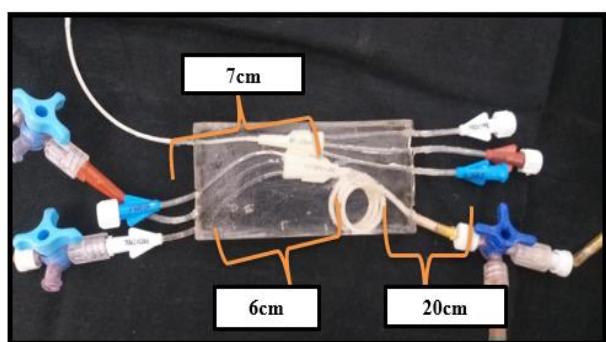


Fig 1. New design microfluidic chip

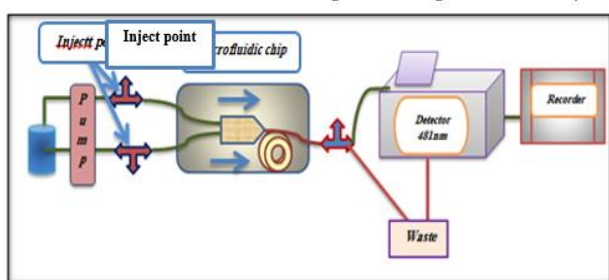


Fig 2. New design of  $\mu$ FIA System.

#### 2.4.2. The stages of work

As shown in Figs. 3, 4, and 5, the measurement of Al (III) was achieved through three processes, comprising the loading of sample and reagent into the microchip and the pumping of a carrier stream of distilled water.

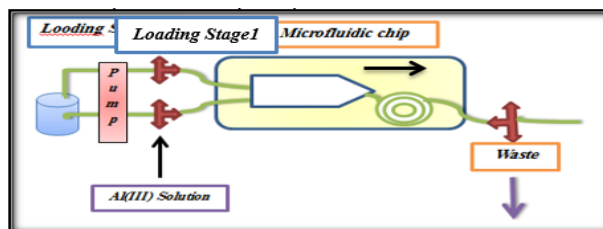


Fig 3. Loading of sample Al (III) solution on microchip

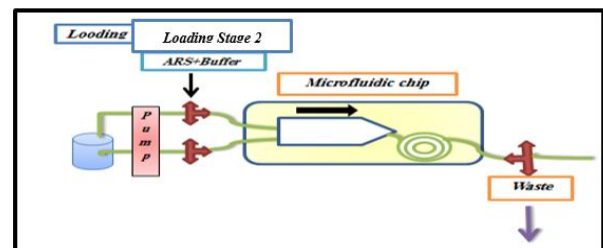


Fig 4. Loading of reagent solution on microchip

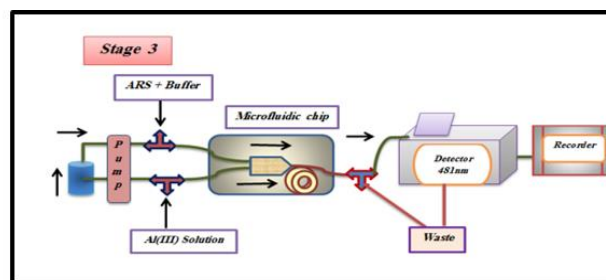


Fig 5: Insertion of the sample and reagent to make the product with the aid of the carrier stream toward the detector and signal recording.

### 2.5. Determination of the maximum absorption wavelength

A UV-Vis spectrum of the Aluminum (III) complex was obtained. As shown in Figure 6, the formed complex solution has maximum absorption at 481nm.

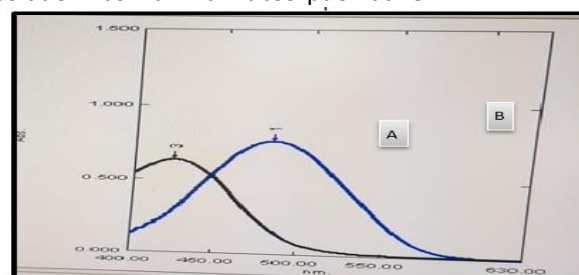


Fig 6: UV-Vis spectrum for Aluminum and reagent in pH= 5, B :of Complex for Al(III), A: of ARS

## 3. Results and Discussion

### 3.1. Effect of flow Rate

The flow rate has an important effect on the peak height over a range of 0.800 - 4.783 ml.min<sup>-1</sup>, and the highest absorbance was at a rate of 4.100 ml.min<sup>-1</sup>, after which the absorbance decreased as in Figure 7.

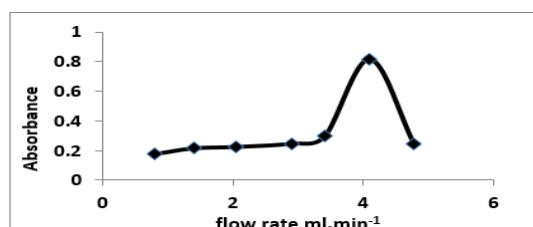


Figure 7: shows the change in absorbance height of flow rate in the  $\mu$ FIA system

### 3.2. Study the effect of the length

The effect of the junction length was studied to load both the reagent and the sample are equal to 13.47 $\mu$ L, 11.77 $\mu$ L respectively. The study showed that the best length was 13.47 $\mu$ L for the ARS volume and 11.77 $\mu$ L for the ion volume.

### 3.3. Effect of ARS concentration

The effect of ARS concentration on the ARS-Al complex formation was investigated in the range of (10<sup>-2</sup> – 10<sup>-7</sup>) mol.mL<sup>-1</sup>. The highest absorbance was observed when the reagent concentration was 0.0001 mol.mL<sup>-1</sup>, as shown in Figure 8.

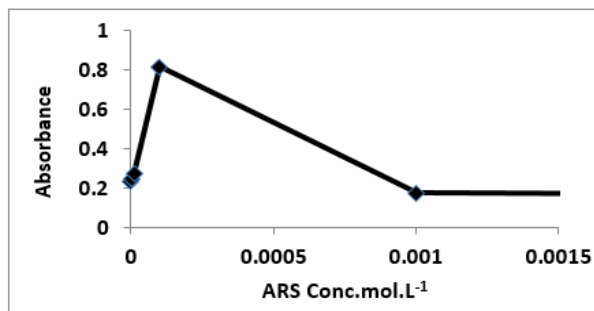


Figure 8: Change of absorbance with ARS concentration in  $\mu$ FIA system.

### 3.4. Calibration Graph

This study was conducted at  $\lambda$  max = 481nm after fixing the optimum conditions, calibration graph of Al (III) was constructed by preparing a series of solutions containing the range of concentrations of it from ( 0.01 - 50)  $\mu$ g.mL<sup>-1</sup>, and the Linearity was (1- 10)  $\mu$ g.mL<sup>-1</sup>. The detection limit LOD was (0.03  $\mu$ g mL<sup>-1</sup>) and the LOQ was (0.120  $\mu$ g. mL<sup>-1</sup>). All results are tabulated in Table (2) and Fig. 9.

Conc.Al(III) $\mu$ g.mL <sup>-1</sup>	Absorbance			mean	SD	RSD%
1	0.098	0.097	0.097	0.097	0.001	1.030
2	0.173	0.174	0.174	0.173	0.001	0.578
3	0.245	0.245	0.246	0.245	0.001	0.408
4	0.319	0.319	0.32	0.319	0.001	0.313
5	0.417	0.417	0.418	0.417	0.001	0.239
6	0.505	0.503	0.501	0.503	0.002	0.398
7	0.591	0.591	0.592	0.591	0.001	0.169
8	0.671	0.671	0.672	0.671	0.001	0.148
9	0.742	0.743	0.743	0.742	0.001	0.134
10	0.837	0.838	0.837	0.837	0.001	0.119

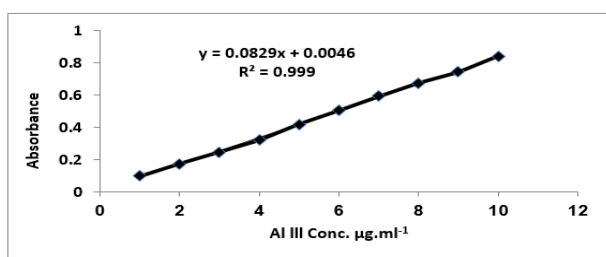
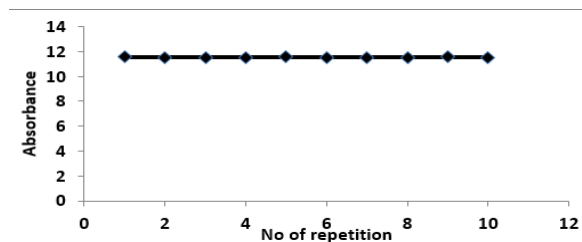


Figure 9: Calibration graph for Aluminum complex by  $\mu$ FIA system

### 3.5. Repeatability

Repetition is the process of injecting successive concentrations of the same sample concentration under the same optimum conditions, where the accuracy and efficiency of the new designed system appear. The effect of iteration was studied at a flow rate of 4.100 ml.min<sup>-1</sup>, the length of the mixing coil was 20 cm, and the aluminum concentration is 5  $\mu$ g.ml<sup>-1</sup>. The number of injection times is 10 (n = 10) As shown in Figure 10,



### 3.6. Efficient of dispersion

The dispersion coefficient (D) is one of the most common experimental parameters that is able to measure the degree of dilution of a sample from the point of injection until it passes through the detector. Dispersion The parameter (D) is easily calculated by the following equation.

$$D = A_0 / A_{max}$$

Where  $A_0$  is the absorption without dispersion outside the  $\mu$ FIA, and  $A_{max}$  is the absorption with dispersion inside the  $\mu$ FIA system. The results are in Table 3 from the result found that: dispersion coefficient value was Limited range.

Al (III) concentration $\mu$ g mL <sup>-1</sup>	Response mm		Dispersion (D) D=A0/Amax
	A <sup>0</sup>	A <sub>max</sub>	
5	0.609	0.417	1.460
10	0.943	0.837	1.126

### 3.7. Effect of foreign ions

The effects of various cations and anions on the determination of Al (III) were studied, such as (Mn<sup>2+</sup>, Fe<sup>3+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Mg<sup>2+</sup>, HPO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, CH<sub>3</sub>COO<sup>-</sup>, and F<sup>-</sup>). All the cations and anions used have no effect on the determination of Al (III).

### 3.8 Applications

The flow injection technique of prepared Aluminum chemical solutions has been effectively used. The collected findings demonstrated a satisfactory recovery, as shown in Table (4). The outcomes achieved were repeatable and precise.

**Table 4. Determination of Aluminum (III) in different pharmaceutical samples by  $\mu$ Flow injection method.**

Pharmaceutical sample	Taken value $\mu\text{g.ml}^{-1}$	Found value $\mu\text{g.ml}^{-1}$	E%	Recovery%*
Maloox plus. Syrup 3.5 mg / 100ml Sonfi-Aventis S.P.A	5	5.2	4.00	104.00
Proolax 225mg/ 5ml Tabuk pharmaceutical manufacturing co	5	4.96	- 0.80	99.20
Acilox plus. 200mg / 1 tab Pioneer	5	4.56	- 8.80	91.20
Maloox plus 200mg / 1 tab Sonfi-Aventis S.P.A	5	4.52	- 9.60	90.40
Acilox plus. Syrup 225 mg/ 5ml Pioneer	5	4.52	- 9.60	90.40
Maloox-MDI 225 mg/ 5 ml Modern Company	5	4.2	- 16.00	84.00
Moxal plus 215mg/ 5ml Julphar Life	5	4.48	- 10.40	89.60
Epicogel 8.1g/ 100ml E.I.P.I.CO.	5	4.88	-2.40	97.60
Antacid 200mg / 1 tab Jedco	5	4.36	-12.80	87.20
Alugel 225 mg/ 5 ml Lincoln	5	4.68	- 6.40	93.60

\*Average of three Times

## 4. Conclusion

This work presents a new and straightforward method for determining Al(III) that has high sensitivity, accuracy, and selectivity (III). Because the laboratory-designed unit and the local unit provide rapid analysis, a wide range of concentrations, and do not require large amounts of chemicals, the design of a micro-flow injection system for the determination of Al(III) does not require expensive equipment in comparison to other technologies.

## References

1. Becaria A, Campbell A, Bondy S. Aluminum as a toxicant. *Toxicology and Industrial Health*. 2002;18(7):309-20. <https://doi.org/10.1191/0748233702th157oa>
2. Khanhuathon Y, Siriangkawut W, Chantiratikul P, Grudpan K. Spectrophotometric method for determination of aluminium content in water and beverage samples employing flow-batch sequential injection system. *Journal of Food Composition and Analysis*. 2015;41:45-53. <https://doi.org/10.1016/j.jfca.2015.02.002>
3. King R, Bisnette M. Organometallic chemistry of the transition metals XXI. Some  $\pi$ -pentamethylcyclopentadienyl derivatives of various transition metals. *Journal of Organometallic Chemistry*. 1967;8(2):287-97. [https://doi.org/10.1016/S0022-328X\(00\)91042-8](https://doi.org/10.1016/S0022-328X(00)91042-8)
4. Schnepf A, Schnöckel H. Metalloid aluminum and gallium clusters: element modifications on the molecular scale? *Angewandte Chemie International Edition*. 2002;41(19):3532-54. [https://doi.org/10.1002/1521-3773\(20021004\)41:19%3C3532::AID-ANIE3532%3E3.0.CO;2-4](https://doi.org/10.1002/1521-3773(20021004)41:19%3C3532::AID-ANIE3532%3E3.0.CO;2-4)
5. Kuenzel M, Bresser D, Kim G-T, Axmann P, Wohlfahrt-Mehrens M, Passerini S. Unveiling and amplifying the benefits of carbon-coated aluminum current collectors for sustainable LiNiO. 5Mn1. 5O<sub>4</sub> cathodes. *ACS Applied Energy*

Materials. 2019;3(1):218-30.

<https://doi.org/10.1021/acsaem.9b01302>

6. Fearnside PM. Environmental and social impacts of hydroelectric dams in Brazilian Amazonia: Implications for the aluminum industry. *World development*. 2016;77:48-65.

<https://doi.org/10.1016/j.worlddev.2015.08.015>

7. Haque M, Sharif A. Study on wear properties of aluminium-silicon piston alloy. *Journal of materials processing technology*. 2001;118(1-3):69-73.

[https://doi.org/10.1016/S0924-0136\(01\)00869-X](https://doi.org/10.1016/S0924-0136(01)00869-X)

8. Modaresi R, Pauliuk S, Løvik AN, Müller DB. Global carbon benefits of material substitution in passenger cars until 2050 and the impact on the steel and aluminum industries. *Environmental science & technology*. 2014;48(18):10776-84.

<https://doi.org/10.1021/es502930w>

9. Jannatin M, Ayu Nabila I, Supriyanto G, Pudjiastuti P. A novel spectrophotometric method for determination of histamine based on its complex reaction with Cu (II) and alizarin red S. *Journal of Chemical Technology and Metallurgy*. 2017;52(6):1045-50.

Available from: [https://dl.uctm.edu/journal/node/j2017-6/5\\_17-20%20Ganden\\_1045-1050.pdf](https://dl.uctm.edu/journal/node/j2017-6/5_17-20%20Ganden_1045-1050.pdf)

10. Alsamarrai KF. Spectrophotometric Assay of Lead in Human Hair Samples by using alizarin red (S) in Samarra area. *J of university of Anbar for pure science*. 2011;5(3). Available from:

<https://www.iasj.net/iasj/download/7fcc3ea8714514d0>

11. Koch MV, VandenBussche KM, Chrisman RW, Chrisman RW. *Micro Instrumentation: For High Throughput Experimentation and Process Intensification - a Tool for PAT*. Wiley, 2007. Available from: <https://books.google.com.pk/books?id=4rdF7AWEbKIC>

12. Nguyen NT, Wereley ST, Shaegh SAM. *Fundamentals and Applications of Microfluidics*, Third Edition. Artech House, 2019. Available from: <https://books.google.com.pk/books?id=h3iFDwAAQBAJ>

13. Zhang J, Yan S, Yuan D, Alici G, Nguyen N-T, Warkiani ME, Li W. *Fundamentals and applications of inertial microfluidics: A review*. *Lab on a Chip*.

- 2016;16(1):10-34. <https://doi.org/10.1039/C5LC01159K>
14. Pawell RS, Taylor RA, Morris KV, Barber TJ. Automating microfluidic part verification. *Microfluidics and Nanofluidics*. 2015;18(4):657-65. <https://doi.org/10.1007/s10404-014-1464-1>
15. Nanda B, Biswal R, Acharya R, Rao J, Pujari P. Determination of aluminium contents in selected food samples by instrumental neutron activation analysis. *Journal of Radioanalytical and Nuclear Chemistry*. 2014;302(3):1471-4. <https://doi.org/10.1007/s10967-014-3569-0>
16. Antunes E, Jacob MV, Brodie G, Schneider PA. Silver removal from aqueous solution by biochar produced from biosolids via microwave pyrolysis. *Journal of environmental management*. 2017;203:264-72. <https://doi.org/10.1016/j.jenvman.2017.07.071>
17. Malik A, Qadir J, Ahmad B, Yau K-LA, Ullah U. QoS in IEEE 802.11-based wireless networks: A contemporary review. *Journal of Network and Computer Applications*. 2015;55:24-46. <https://doi.org/10.1016/j.jnca.2015.04.016>
18. Mohapatra D, Hong-In K, Nam C-W, Park K-H. Liquid–liquid extraction of aluminium (III) from mixed

- sulphate solutions using sodium salts of Cyanex 272 and D2EHPA. *Separation and purification technology*. 2007;56(3):311-8. <https://doi.org/10.1016/j.seppur.2007.02.017>
19. Shirkhanloo H, Abbasabadi MK, Hosseini F, Zarandi AF. Nanographene oxide modified phenyl methanethiol nanomagnetic composite for rapid separation of aluminum in wastewaters, foods, and vegetable samples by microwave dispersive magnetic micro solid-phase extraction. *Food Chemistry*. 2021;347:129042. <https://doi.org/10.1016/j.foodchem.2021.129042>
20. Supian SM, Ling TL, Heng LY, Chong KF. Quantitative determination of Al (III) ion by using Alizarin Red S including its microspheres optical sensing material. *Analytical Methods*. 2013;5(10):2602-9. <https://doi.org/10.1039/C3AY40238J>
21. Abd FF, Ali KJ. DESIGN OF A NEW MICROFLUIDIC CHIP FOR THE DETERMINATION OF SELENIUM (IV) USING DITHIAZONE AS REAGENT AS A MODEL OF BIOCHEMICAL APPLICATION. Available from: <https://www.researchgate.net/publication/348356858>