

Designing Home-made Microfluidic System for the Determination of Magnesium Ion in Natural Water

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Abstract: The homemade microfluidic FI spectrophotometric system was designed for the estimation of magnesium ion in water samples. A double channels microfluidic chip was designed with 40 μ L volume and 5 cm length. The proposed system was supplied with two Arduino microcontrollers types UNO and mega. The first one was used for controlling a homemade micro peristaltic pump to drive the samples and chemical reagents to the spectrophotometer equipped with 7 μ L flow cell volume. The other type was the Mega which was used as a data logger to record the results as peaks by corresponding to concentration using a homemade software signal to peak program which was installed on Microsoft Excel 2010. The linearity for this method was in the range 5-35 μ g/ml, the regression coefficient of seven points and the relative standard deviation for ten injections of 25 μ g/ml magnesium was 0.9994 and 0.36%, respectively. The detection limit was 0.3125 μ g/ml and the sample output was 150 s/h. Each sample consumed 44.396 μ l of chemical reagents; therefore, 150 samples consumed 6.664 ml of chemical reagents. The proposed system will provide rapid, low cost, low consumption of sample and chemical reagents with low waste, so, this system can be called an Eco-friendly system.

Keywords: Microfluidic- Flow Injection Analysis, Arduino, UNO controller, Mega controller, Magnesium, Spectrophotometer

Microfluidic is a system that merges one or more analytical processes in a single or double microchip with an extremely small volume of fluids has microchannels ranged 10 -100 micrometers (Watts and Charlotte 2012) and is most commonly used in analytical analysis due to numerous advantages such as very rapid mixing occurs between sample and reagents and the short microchannels distances within such systems. The volume of these channels is very small which means that reaction conditions can be achieved with very small reagent quantities, therefore, leads to reduce waste volume (Andrew et al 2003, Pravinraj and Patrikar 2019). The microfluidic technique found a lot of applications in many such as chemical analysis, DNA labyrinths, environmental analysis, single-cell detection, medical diagnostics and pharmaceutical analysis (Foan 2018, Maguire et al 2018, Tavakoli 2019). Additionally, wide applications are in environmental analysis, especially in water analysis. The microfluidic technique has achieved a lot of green analytical chemistry goals like reducing chemical reagents, and sample consumption. It is also inherent the flow analysis characterizes for instance the high reproducibility, controlling of dispersion, and increasing sample throughput (Amenta et al 2008). Therefore, microfluidic can offer a very suitable detection system for this purpose. Recently, a homemade micro FIA semi-automated system was designing and build-up with the benefits of

microcontrollers for the determination of phosphate in soft drinks, chloride and nitrate determination in natural water (Al-Jorani and Al-Sowdani 2021). This study intends to design a home-made microfluidic system can be constructed to offer an Eco-friendly system for low consumption of chemical reagents, high throughput, reproducible and accurate determination of magnesium ion in water samples.

MATERIAL AND METHODS

Deionized water was utilized in the preparation of all solutions and all chemicals were having a high purity. Magnesium ion standard solution 100 μ g/ml was prepared by dissolved 1.025g of magnesium sulfate heptahydrate $MgSO_4 \cdot 7H_2O$ (CDH) in 1liter of double-distilled water. Eriochrome Black T Solution (Thomas baker) 0.3%w/v was prepared by dissolved 1.5g in 500 ml double distilled water. The buffer solution was prepared by dissolved 7 g of NH_4Cl (CDH) in water, then adds 57 mL of concentrated NH_3 solution (Scharlau), and dilutes the mix solution by double deionized water to 1 liter.

Design of Microfluidic FI system: The lab-made microfluidic FI spectrophotometric system was equipped with two microcontroller types Arduino UNO and Mega (Fig. 1). The UNO was used to control the flow rate of the homemade micro peristaltic pump at the range of 0.4-5.0 ml/min. The Mega type was utilized to transform the analogue signal to

digital signal one by connecting to a PC equipped with the homemade signal to peak program and Microsoft Excel 2010 program. A spectrophotometer was set with a 7 μ L microflow cell (QS Hellma) was used to measure the absorbance of the colored products. An injection valve was used to inject the sample in the range of 10-22 μ L manually. The most important components of a microfluidic FI system is the microchip which was fabricated in our lab. This chip contains double channels that had 40 μ L volume and 5cm length for each

channel which was focusing on reducing the consumption of chemical reagents and sample volume. The made-up microfluidic chip consists of two layers which were pasted together by using epoxy adhesive and the micro PTFE tubes were fixed to the microchip using an epoxy adhesive. The first microchannel was used to pass on buffer solution by using 0.2mm PTFE tubes where magnesium ion samples are injected while merge with the other channel carries on Eriochrome black T reagent to form the pink complex (Fig. 2).

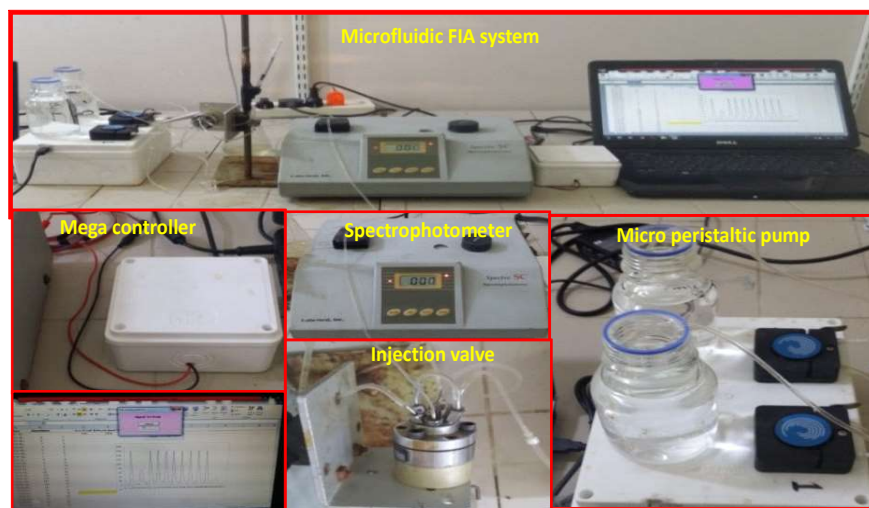


Fig. 1a. Home-made microfluidic FI spectrophotometric system which was designed

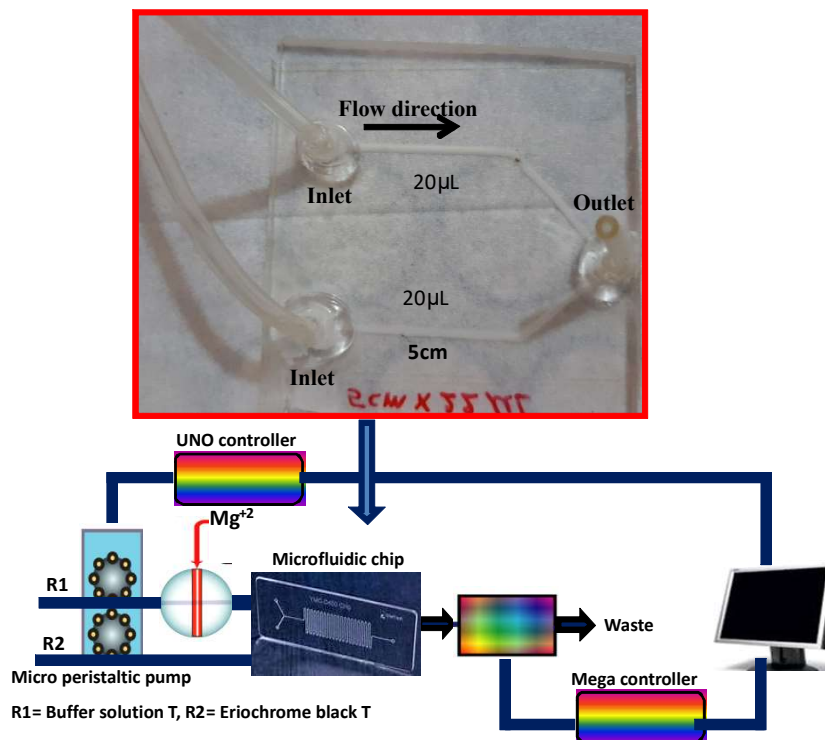


Fig. 1b. Home-made microfluidic FI spectrophotometric system

Subsequently, the absorbance of the pink complex was recorded at 560nm (Fig. 3) as peak height which corresponding to the concentration of magnesium ion in the injected sample.

RESULTS AND DISCUSSION

The spectrum of a formed complex and magnesium with Eriochrome Black T in an alkaline medium (pH=12) determined by a scanning spectrophotometer (Spv-720 (Fig. 2 and Fig. 3). The maximum absorbance of the pink complex was at 560 nm which was used throughout this study. The microfluidic FI system was optimized for rapid and sensitive determination of magnesium ion by conducting a series of experiments. The main peak height was the average of three replicates. Firstly, the influence of pH on peak height was estimated in the range 7-13 (Table 1 and Fig. 4). The results showed that peak height increased with increasing the pH to extent 12. The peak height was reduced, pH=12 was chosen for subsequent studies to provide the greatest sensitivity. Flow rate is one of the important physical variables in microfluidic systems which must be fit for designing the chip. The total flow rate effect on 25 $\mu\text{g/ml}$ magnesium ion ranged 1.0-2.5 ml/min. The peak height decreases with an increasing total flow rate. The low total flow rate permits the pink formed complex to stay most time in the microflow cell, which leads to more sensitivity (Al-Sowdani 2009). The 1.0 ml/min was selected as the best total flow rate for later experiments (Table 2 and Fig. 5). The injected sample volume was studied in the range of 10-26 μL . the sensitivity increases progressively with the increasing sample injected consequently, which thought due to a decrease in the dispersion of the proposed system (Al-Sowdani et al 2016) Therefore, 26 μL of sample injected was selected for the next experiments to get high sample throughput and appropriate sensitivity (Table 3 and Fig. 6). The effect of Eriochrome black T concentration which was studied in the range 0.05-0.25%w/v. The sensitivity increase with the increase of EBT concentration due to the increase of product complex (Khadija et al 2016). Therefore, a 0.25w/v% was selected in the future experiment to decrease the analysis time and to produce a high sensitivity (Table 4 and Fig. 7).

Standard calibration curve: The calibration curve for magnesium ion was obtained by the proposed system (Table 5). Linearity was in the range 5-35 $\mu\text{g/ml}$ (Table 6 and Fig. 8a, b). A regression coefficient (R^2) for seven points was 0.9994 and the relative standard deviation for 10 injections of 20 $\mu\text{g/ml}$ magnesium was 0.36% (Fig. 8c). The detection limit was 0.3125 $\mu\text{g/ml}$ and the dispersion coefficient of the proposed system was 1.21 (Fig. 9). The sample throughput was 150 s/h. Each sample consumed 44.396 μl from the

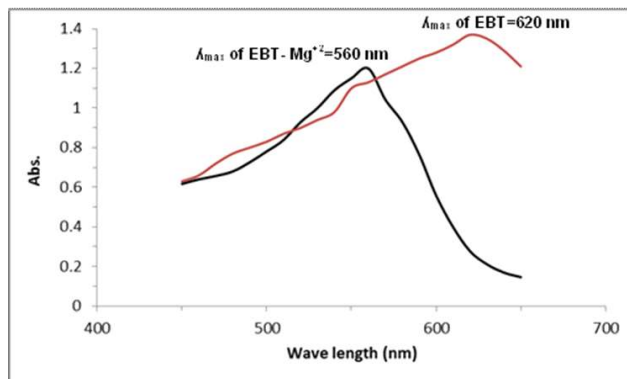


Fig. 2. Spectrum of magnesium with Eriochrome Black T

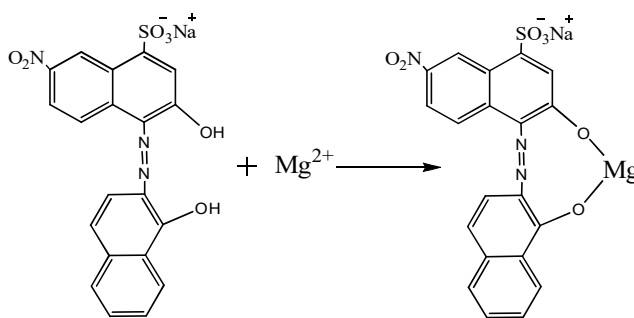


Fig. 3. EBT-Mg²⁺ complex

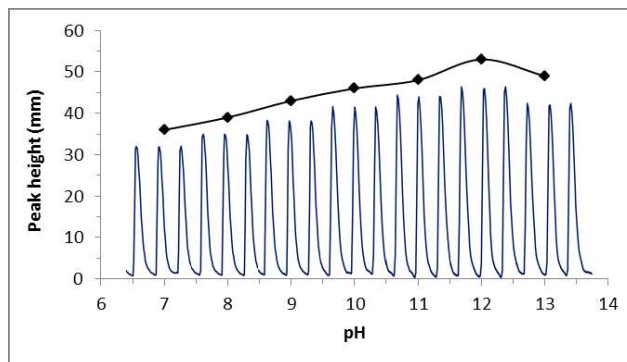


Fig. 4. Effect of pH on peak height of 25 $\mu\text{g/ml}$ Magnesium ion

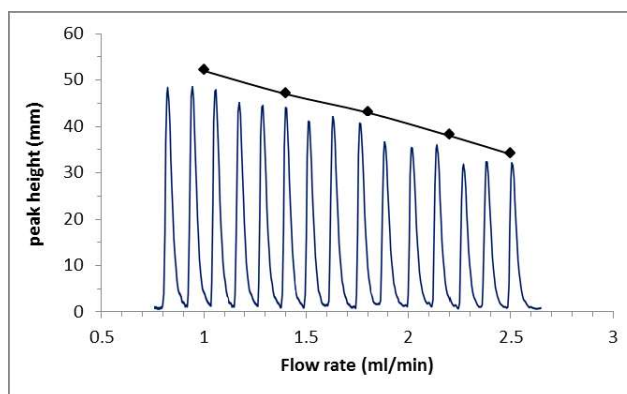


Fig. 5. Influence of the total flow rate on peak height of 25 $\mu\text{g/ml}$ Magnesium ion

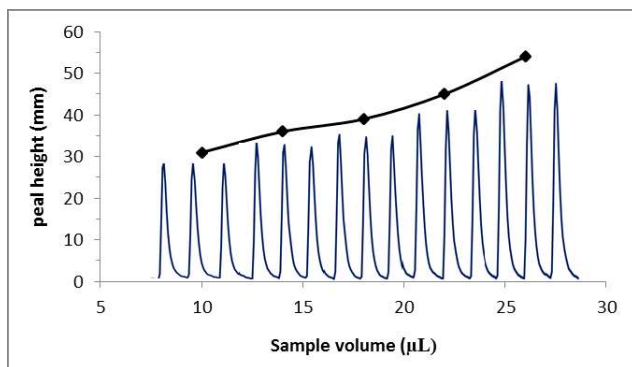


Fig. 6. Effect of the sample volume injected on peak height of 25µg/ml Magnesium ion

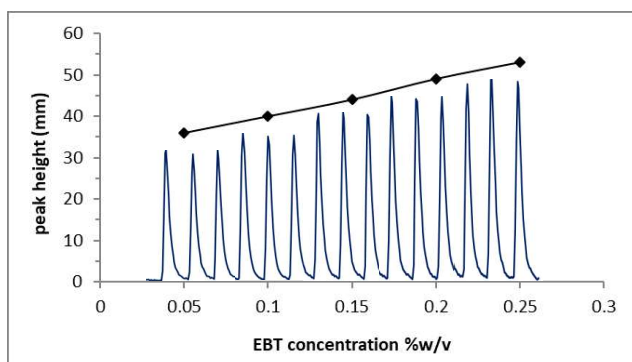


Fig. 7. Effect of EBT concentration on peak height of 25µg/ml magnesium ion

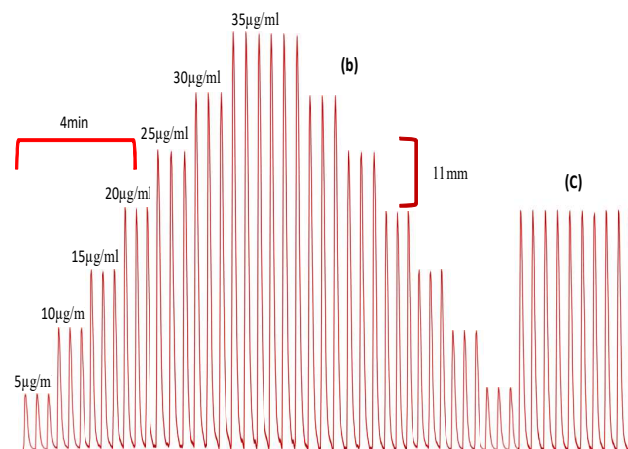
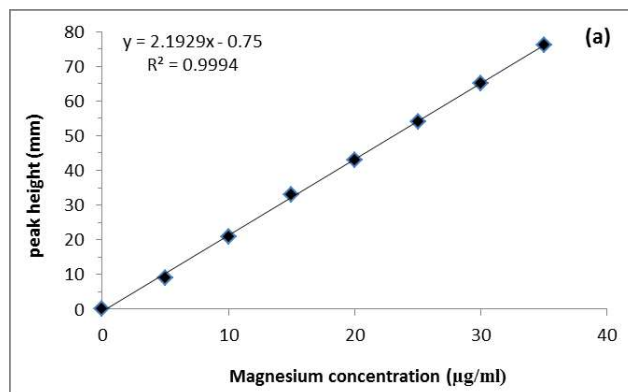


Fig. 8. (a). Standard calibration curve of magnesium ion estimation (b) Peaks of Mg^{2+} Standards (c) 10 injections of 25 µg/ml Mg^{2+} standards

Table 1. Effect of the pH on the peak height*

pH value	Peak height (mm)			Mean \pm RSD (%)
7.0	36.30	36.30	36.20	36.26 \pm 0.1608
8.0	39.20	39.20	39.10	39.16 \pm 0.1489
9.0	43.30	43.30	43.10	43.23 \pm 0.2672
10.0	46.40	46.40	46.30	46.36 \pm 0.1257
11.0	48.20	48.10	48.00	48.10 \pm 0.2079
12.0	52.40	52.20	52.40	52.33 \pm 0.2207
13.0	49.3	49.3	49.2	49.26 \pm 0.2011

* Mg^{2+} conc. = 25 µg/ml, Total flow rate = 1.0ml/min, sample volume injected = 26µL, EBT conc. = 0.25% w/v

Table 2. Influence of the total flow rate on the peak height *

Total flow rate (ml/min)	Peak height (mm)			Mean \pm RSD (%)
1.0	52.50	52.25	52.2	52.33 \pm 0.2759
1.4	47.50	47.00	47.0	47.16 \pm 0.6121
1.8	43.00	43.50	43.5	43.33 \pm 0.6660
2.2	38.50	38.00	38.5	38.33 \pm 0.7532
2.5	34.00	34.50	34.5	34.33 \pm 0.8409

* Mg^{2+} conc. = 25 µg/ml, sample volume = 26µL, EBT conc. = 0.25% w/v, pH = 12

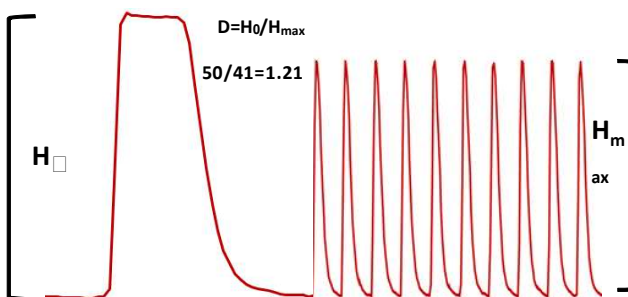


Fig. 9. Dispersion coefficient of the proposed system

Table 3. Effect of the sample volume injected on the peak height*

Injected sample volume µL	Peak height (mm)			Mean \pm RSD (%)
10	31.20	31.20	31.00	31.13 \pm 0.3711
14	36.60	36.50	36.30	36.46 \pm 0.4195
18	39.40	39.20	39.00	39.20 \pm 0.5102
22	45.30	45.20	45.20	45.23 \pm 0.1279
26	54.60	54.40	54.50	54.50 \pm 0.1834

* Mg^{2+} conc. = 25 µg/ml, Total flow rate = 1.0ml/min, EBT conc. = 0.25% w/v, pH = 12

chemicals as a result, 150 samples required 6.664 ml from the chemical reagents

Analytical applications: To test the capability of the microfluidic FI system for determination magnesium ion concentrations in water samples, 10 water samples were taken from Shatt Al-Arab water. The accuracy of proposed system was evaluated by comparing the obtained results with a classical method which was shown a good agreement between the two methods (Table 7). These results indicated that the microfluidic FI system can be used for several applications to determine magnesium ion in different samples. The proposed system sensitivity was compared

Table 4. Effect of EBT concentration on the peak height *

Injected sample volume μL	Peak height (mm)			Mean \pm RSD (%)
0.05	36.40	36.20	36.30	36.30 \pm 0.1947
0.1	40.30	40.20	40.20	40.26 \pm 0.1648
0.15	44.20	44.20	44.00	44.13 \pm 0.2618
0.2	49.30	49.20	49.20	49.23 \pm 0.1175
0.25	53.00	53.20	53.10	53.10 \pm 0.1883

*Mg²⁺ conc. = 25 $\mu\text{g/ml}$, Total flow rate =1.0ml/min, sample volume injected = 26 μL , pH = 12

Table 6. Standard calibration curve of magnesium ion estimation

Magnesium ion conc. ($\mu\text{g/ml}$)	Peak height (mm)			Mean \pm RSD (%)
5	9.3	9.3	9.2	9.26 \pm 0.6296
10	21.1	21.1	21.0	21.06 \pm 0.2768
15	33.3	33.2	33.3	33.26 \pm 0.1753
20	43.4	43.3	43.4	43.36 \pm 0.1344
25	54.3	54.2	54.2	54.23 \pm 0.1977
30	65.4	65.3	65.3	65.33 \pm 0.1641
35	76.3	76.3	76.2	76.26 \pm 0.0764

with some previously reported analytical methods for estimation of magnesium in (Table 8).

Interferences study: Eriochrome Black T is most commonly used as a chemical reagent for the estimation of many ions but is not a highly selective reagent. The Table 9 and Figure 10 show the results of 50, 100, and 1000 folds of selected interferences cations and anions for 25 $\mu\text{g/ml}$ magnesium estimation by home-made microfluidic FI system. The aluminum (III), Nickel (II), calcium (II), iron (III), copper (II),

Table 5. Optimum conditions for Mg²⁺ determinations

Parameter	Value
Microfluidic chip volume with two channels	40 μL
Total flow rate	1.0 ml/min
Sample volume	26 μL
EBT concentration	0.25 %w/v
pH	12
Rest of the manifold tube diameter	0.2 mm

Table 7. Magnesium ion concentrations in the selected sits

Sample collection sites	Magnesium ion concentrations ($\mu\text{g/ml}$)	
	Microfluidic FI method \pm R.S.D (%)	Classical method \pm R.S.D (%)
Qurna	120 \pm 0.3786	118.5 \pm 0.3273
Qurna 2	130 \pm 0.2832	127.9 \pm 0.2984
Al-sharsh	65 \pm 0.4329	66.0 \pm 0.3769
Al-deer	60 \pm 0.2650	64.0 \pm 0.1286
Saad bridge	60 \pm 0.2654	63 \pm 0.4872
Qurmat ail	120 \pm 0.1765	123 \pm 0.5197
Ashar	150 \pm 0.2532	147 \pm 0.2804
Abual Khasib	200 \pm 0.2359	202 \pm 0.4321
Fao	300 \pm 0.4987	298 \pm 0.2872
Khour al-zubair	350 \pm 0.3476	345 \pm 0.1875

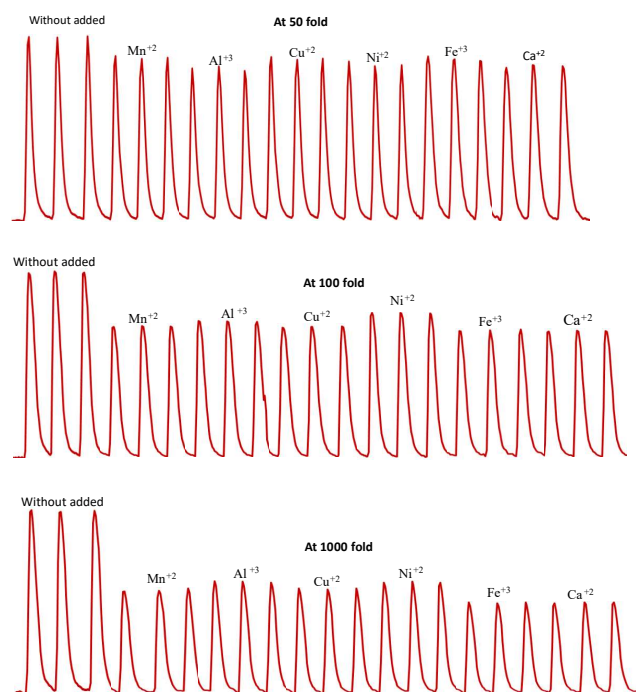
Table 8. Comparison of the proposed system sensitivity with previously reported analytical method

Methods	Reagent	Samples	Detection limit	Linearity	Ref.
Flou.-SIA	8-hydroxyquinoline-5-sulfonic acid	Natural water	12 $\mu\text{g/l}$	up to 1.2 mg/l	De-Armas et al 2000
voltammetry	Thiopentone sodium (TPS)	Water samples	0.14 $\mu\text{g/l}$	0.14–2.16 $\mu\text{g/l}$	Othman 2004
Capillary zone electrophoresis	EDTA	Seawater	0.13 mg/l	up to 20.0 mg/l	Keiichi and Kazuo 1996
FIA	XYLYLAZO VIOLET I	Water samples	2 \times 10 ⁻⁶ M	2 \times 10 ⁻⁶ -1.2 \times 10 ⁻⁴ M	Yunhua et al 1995
SIA-Titration	calmagite and EDTA	Surface water	0.1mg/l	0.5–5.0mg/l	Brett 1997
Classical SP.	Eriochrome Black T	Drinking water	0.012 $\mu\text{g mL}$	0.05-1.2 $\mu\text{g/ mL}$	Ramazan and Ibrahim 2009
HPLC	Mobil phase: o-cresolphthalein	Water samples	0.05mg/l	-	Brett 1997
Microfluidic	Eriochrome Black T	Water samples	0.3125 $\mu\text{g/ml}$	5.0-35 $\mu\text{g/ml}$	Current study

Flou.-SIA= Fluorimetric sequential injection, EDTA=Ethylene diamine tetraacetic acid, SP-SIA=spectrophotometer -sequential injection analysis, HPLC= High performance liquid chromatography

Table 9. Interferences study on magnesium ion estimation

Ions	Add	Peak height (mm) at folds			
		Without added	50	100	1000
Manganese (II)	MnCl ₂	45	39	32	25
Aluminum (III)	AlCl ₃	46	37	33	26
Copper (II)	CuSO ₄ .5H ₂ O	44	39	31	25
Iron (III)	FeCl ₃	45	37	30	22
Calcium (II)	CaCl ₂	43	39	30	22
Nickel (II)	Ni(NO ₃) ₂	45	38	44	27
Phosphate	KH ₂ PO ₄	45	44	42	42
Chloride	NH ₄ Cl	44	45	43	40
Sulfate	ZnSO ₄ .5H ₂ O	43	46	43	42
Fluoride	Na ₂ SiF ₆	44	44	42	41
Nitrite	NaNO ₂	43	45	44	44
Nitrate	NaNO ₃	43	44	43	43
Bromide	KBr	46	43	42	41

**Fig. 10.** Interferences study of magnesium determination

zinc (II), and manganese (II) ions were interfered obviously up to 50. The influence of cations can be removed by using masking reagent solutions such as EDTA, sodium citrate, and potassium cyanide for manganese (II), copper (II), calcium (II), zinc (II), and aluminum (III), NaF for iron (III) and aluminum (III), triethanolamine for only iron (III). The chloride, bromide, sulfate, nitrite, nitrate, phosphate, and fluoride ions as anionic interfering species did not interfere in the determination of 25 µg/ml Mg (II) in natural water.

CONCLUSION

The homemade semi-automated microfluidic FI was designed for analyzing magnesium ion in water samples. This proposed system can be classified as Eco friendly system and can be easily constructing from simple, cost effective and affordable components in local market. This semi-automated system was superior to classical procedure for magnesium ion determination.

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