Determination of Zinc (II) Ion Using Dithizone by Flow Injection and Sequential Injection Techniques

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Abstract

This determinates Zinc (II) ion in variably samples by using methods flow injection and sequential injection systems which laboratory. The FIA and SIA systems depend on the base reaction of Zinc (II) ion with dithizone complex in aqueous phase in the presence of SDS anionic (sodium dodecyl sulphate) at pH=5 with absorption maximum at 565 nm. The factors (physical and chemical) effecting on the determination such as flow rats, reaction coil length, the volume of reagent (dithizone), the volume of sample, interference, the concentration of dithizone also. Attended the calibration curve and studied dispersion coefficient, reproducibility, application. Compared results methods FIA and SIA consecutively for determination of Zinc (II) by dithizone, the linear range was (2-10 mg/l), (1-15 mg/l), at sampling rate 70, 64 sample per hour, the detection limits (1.6746 mg/l), (0.1934 mg/l) for FIA and SIA respectively. Relative standard deviation for (10 mg/l), n=10 were found (0.8491 mg/l) for FIA and for SIA (0.5089 mg/l). Dispersion coefficient also has been studied in these methods.

Keywords: Flow injection; Sequential injection; Dithizone; Zinc (II) ion

Introduction

Zinc (II) ion is a metal of great nutritional importance and is the second element after iron in terms of abundance in the human body. The importance of the ore has been known since 1960, as the micronutrient is required for the effectiveness of more than 300 enzymes and 1000 of the necessary transcription factors also show its importance in controlling the expression The gene, which plays an important role in the work of amino acids and the manufacture of proteins and replication of cells as well as the growth and repair of the tissue is considered Zinc (II) ion as antioxidants and stability of the membranes indicate that it has the ability to resolve the free radical caused by injury during infections [1-5], the main of Zinc (II) ion deficiency in most cases may result from heavy dependence on foods with little Zinc (II) ion or low absorption. High fat and acid content in the bowel that prevents absorption of Zinc (II) ion [6,7]. Deficiency occurs in various conditions like malformation syndrome, cirrhosis of liver. The best food sources of Zinc (II) ion include meat-based products, especially the most abundant meat, such as chicken, beef, rabbit meat, scallops, lamb found in cytosol, vesicles, organelles and in the

nucleus [8]. Zinc (II) ion has relatively low melting point (419.5°C) and boiling point (907°C) [9-11]. The first determination of Zinc (II) ion-dithizone complex, in aqueous phase is, in the presence of SDS anionic (sodium dodecyl sulphate).

Dithizone was green- bluish powder is dissolved in ethanol, methanol, chloroform and carbon tetrachloride. Dithizone or diphenyl thaio carbazone, which symbolizes D, which was discovered by Amel Fisher and was found in the form of saline clusters known as dithizones, which are the same colors in solutions. Ten years ago, Fischer began using dithizone as an analytical detector and has been used in the detection of many minerals, which is known to be able to link with ions and other elements of the physical properties be a crystalline blackish blue color of blue $C_6H_5N=NCSNHNHC_6H_5e$, which is a sulfur-containing compound and is a good ligand, dithizone is a widely used compound in volume measurement methods.

Irrigation is insoluble in alkaline solvent and water if the container was impurities due to be salt, but if it was pure good solubility in organic solvents only, such as chloroform, carbon tetrachloride. Dithizone has many applications in the process of extracting elements such as silver, copper, and lead and was used with Zinc (II) ion using carbon tetrachloride at pH (5.5) [12,13]. Its medical benefits are its ability to attack toxic cells in the prostate, the possibility of contact with chemotherapy and its attack on prostate cancer [14]. Zinc (II) ion estimated by a number of ways, including using the method of Flame Atomic Absorption Spectrophotometry [15], Sequential Injection System [16], Chromatography Coupled with Plasma Optical Emission Spectrometry (ICP-OES) [17], Capillary Electrophoresis with Contactless Conductivity Detection [18] and Adsorptive Stripping Voltammetry at A Mercury Film Electrode [19] etc.

Experimental

Apparatus

Spectrophotometer laboring single beam, spectrophotometer Shimadzu UV-1700, USA, pipes load of Teflon, flow cell volume of 450 μ pH meter, peristaltic pump Germany, analytical balance sensitive Denver instrument, Recorder Pen Siemens C1032 Hitter Ardeas 51 homemade valve, Ismatic.

Chemicals

- The standard stock 1000 mg/l of Zinc (II) ion prepared by dissolving 0.2086 g of Zinc chloride $ZnCl_2$ in water and dilute the solution with distilled water to 100 ml.
- 1×10^{-4} mol/l of dithizone solution was prepared by dissolving 0.00265 g of dithizone in 100 ml of ethanol in the volumetric flask.
- The buffer solution of prepared PH=5 dissolve 0.4 g of Sodom acetate in water, and dissolve 0.3 g from acetic acid in water, and dilute the solution with water to 50 ml.
- SDS solution 0.01% prepared by dissolved 0.01 g of SDS in 100 ml water.
- Trtionx-100 solution 0.01% prepared by dissolved 0.01 g of Trtionx-100 in 100 ml water.

Results and Discussion

Determination of the wavelength for maximum absorption

Defining of the wavelength for maximum absorption by use Ultraviolet-visible spectroscopy was used to determine the optimum condition for the Zinc (II) ion complex and the result are shown in FIG. 1. The λ max of complex was 565 nm.
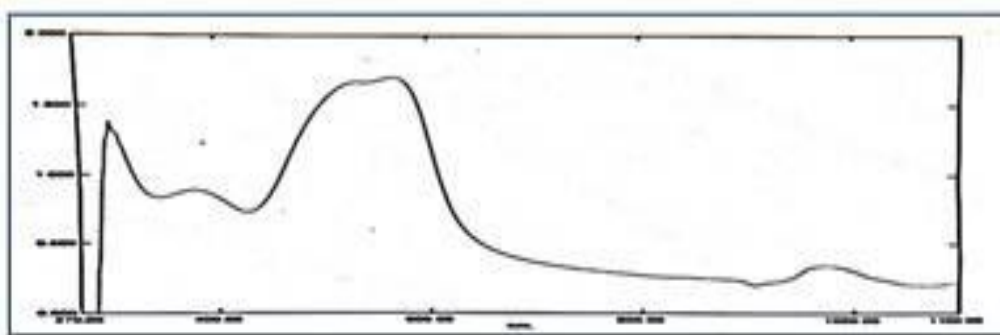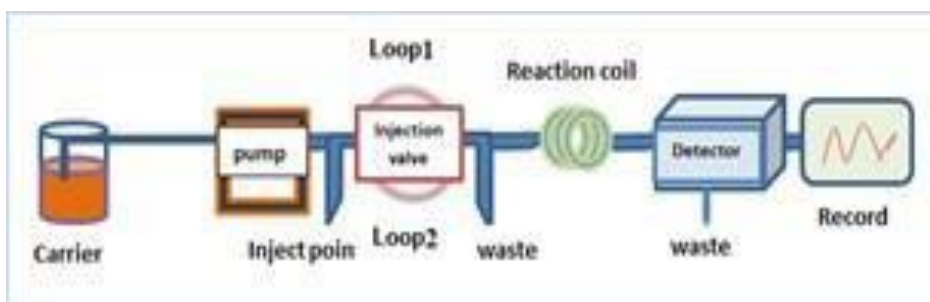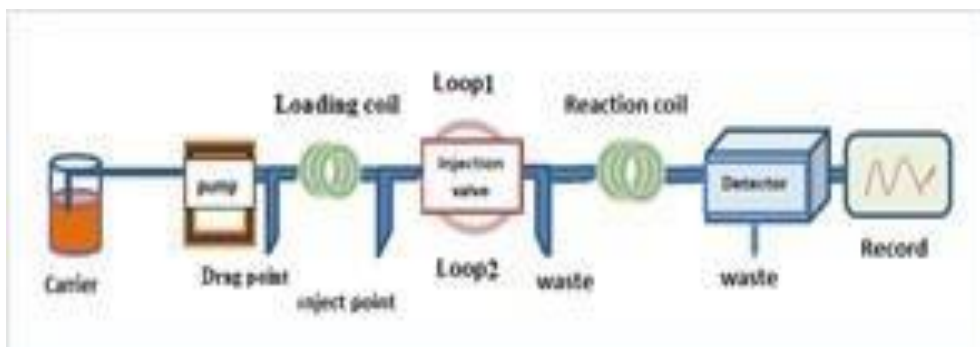
FIG. 1. **UV-VIS spectroscopy for Zinc (II) ion complex with dithizone at pH=5.**

Design of FIA and SIA units

The difference parameters affecting the unit have been achieving a final method evaluation. The following results allow the operator choose difference operation condition. Used new designs as shown in the DESIGN 1 and 2.

DESIGN 1. **New design of FIA unit.**

DESIGN 2. **New design of SIA unit.**

Study effecting type medium micelle

Using two types from the medium the micelle them Triton X-100 and SDS anionic (sodium dodecyl sulphate) with concentration 0.01 mol/l, (TABLE 1), demonstrate using medium from SDS give the best null in form and height.

TABLE 1. **Effect of type medium micelle on peak height at Zinc (II) ion conc.=10 mg/l, Reaction coil length=50 cm, Dithizon conc.=5 × 10⁻⁵ mol/l, Sample volume=157.0 μl, Reagent volume=141.3 μl, SDS, TritonX-100=0.01% in FIA unit.**

Type of medium	Peak height cm			Mean	SD	RSD%
With out	3.0111	3.0900	3.0130	3.0380	0.04123	1.3571
With SDS	3.0300	3.0130	3.0830	3.4633	0.0717	2.0702
With TritonX-100	2.9730	2.9100	2.9990	2.9606	0.0458	1.5469

Study effecting concentration of SDS anionic (sodium dodecyl sulphate)

After determinable environment from SDS chose concentrations in the range of (0.05-0.002) mol/l, (TABLE 2 and FIG. 2), the concentration 0.01% giving the best results.

TABLE 2. **Effect of concentration of SDS on peak height at Zinc (II) ion conc.=10 mg/l, Reaction coil length=50 cm, Dithizon conc.=1 × 10⁻⁵ mol/l, Sample volume=157.0 μl, Reagent volume=141.3 μL, SDS=0.01%, flow rate=9.000 ml/min in FIA unit.**

Conc. SDS mol/l	Peak height cm			Mean	SDS	RSD%
0.002	3.0070	3.0070	3.0070	3.0070	0.0000	0.0000
0.01	3.5000	3.5100	3.3800	3.4633	0.0717	2.0702
0.05	3.3590	3.3120	3.3850	3.3520	0.03605	1.0754

Effect of the flow rate

The effect of the flow rat on the peak height was the lesson in the range of 1-13 ml/min (TABLES 3 and 4 and FIG. 2 and 3) show that, the flow rate was 11.20 ml/min, as optimizing rate after that the height of peak was reduced due to declining the sensitivity of measurement in height flow rate because the reaction was no attaining when increased the flow rate [20].

TABLE 3. **Effect of the flow rate on peak height at Zinc (II) ion conc.=10 mg/l, Reaction coil length=50 cm, Dithizon conc.=5 × 10⁻⁵ mol/l, Sample volume=157.0 μl, Reagent volume=141.3 μL, SDS=0.01% in FIA unit.**

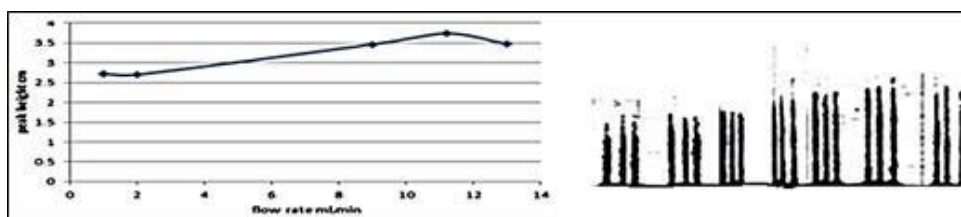| Flow rate ml/min	Peak height (cm)			Mean	SD	RSD%
1.00	2.6470	2.6000	2.6583	2.6351	0.0300	1.1384
2.00	2.7200	2.7200	2.7600	2.7333	0.0300	1.0975
5.600	2.8710	2.900	2.8110	2.8606	0.0447	1.5626
7.500	3.103	3.1176	3.1870	3.1358	0.0441	1.4063
9.00	3.5000	3.5100	3.3800	3.4633	0.0717	2.0702
11.20	3.7290	3.7020	3.7900	3.7403	0.1516	4.0531
13.00	3.5500	3.4700	3.3100	3.4266	0.1234	3.6012

FIG. 2. **Change of peak height with flow rate in FIA unit.**

TABLE 4. **Effect of the reaction coil length on peak height at Zinc (II) ion conc.=10 mg/l, Dithizon conc.=5 × 10^{-5} mol/l, Sample volume=157.0 μl, Reagent volume=141.3 μl, SDS=0.01% in FIA unit.**

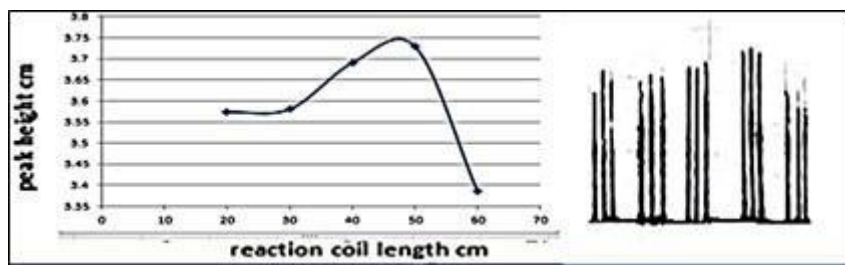| Reaction coil length (cm)	Peak height (cm)			Mean	SD	RSD%
03	3.4900	3.6400	3.5900	3.5733	0.0758	2.1212
03	3.5608	3.5900	3.5900	3.58026	3.0122	0.3407
03	3.6600	3.7500	3.6600	3.6900	0.0324	0.8780
03	3.7290	3.7020	3.7900	3.7403	0.1516	4.0531
03	3.4560	3.3990	3.3000	3.3850	0.0781	2.3072

FIG. 3. **Change of peak height with reaction coil length in FIA unit.**

Effect of the sample volume in FIA

The influence of the different volume 117.75-235.5 μl of samples was observed sample volume that exhausted the greatest peak height was found to be 157.0 μl and it was chosen as the optimum (TABLE 5, FIG. 4).

TABLE 5. **Effect of the Sample volume on peak height at Zinc (II) conc.=10 mg/l. Reaction coil length=50 cm, Dithizon conc.=5 × 10^{-5} mol/l, Reagent volume=157.0 μl, SDS=0.01%, Flow rate=11.20 ml/min, in FIA unit.**

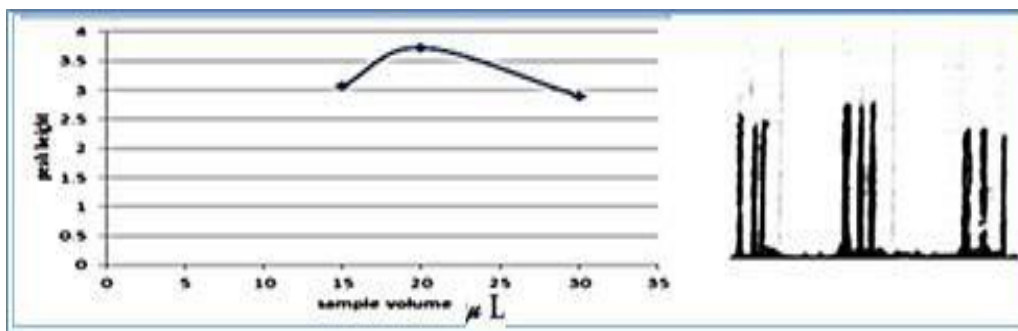| V of Zinc (II) ion μl	Peak height cm			Mean	SD	RSD%
117.75	3.2490	3.0780	2.8740	3.0670	0.1327	4.3267
157.0	3.7290	3.7900	3.7020	3.7290	0.1516	4.0531
235.5	2.9440	088003	088383	088880	0.0353	1.2178

FIG. 4. **Change of peak height with sample volume in FIA unit.**

Effect of the reagent volume in FIA

The influence of the different volume 78.50-157.0 µl, reagent volume that exhausted the greatest peak height was found to be 141.3 µL and it was chosen as the optimum (TABLE 6, FIG. 5).

TABLE 6. **Effect of the reagent volume on peak height at Zinc (II) ion conc.=10 mg/l, Reaction coil length)=50 cm, Dithizon conc.=5 × 10^{-5} mol/l, Sample volume=157.0 µl, SDS=0.01%, Flow rate=11.20 ml/min in FIA unit.**

V of dithizone µl	Peak height cm			Mean	SD	RSD%
78.50	3.4350	3.3480	3.3350	3.3726	0.0538	1.5936
141.3	3.7290	3.7020	3.7900	3.7403	0.1516	4.0531
157.0	2.8070	2.9080	2.9350	2.8833	0.0670	2.3237

Effect of the reagent concentration

The concentration of the reagent was various in the range ($0.5 \times 10^{-5} \times 10^{-6} \times 10^{-5}$) mol/l in FIA in order to maximize the peak height. (TABLE 7 and FIG. 6) have shown the effect of reagent concentration on the peak height of Zinc (II) ion. The maximum peak height was obtained with the reagent, the peak height lowered and form double peak, therefore, the 5×10^{-5} mol/l reagents was chosen for further work.
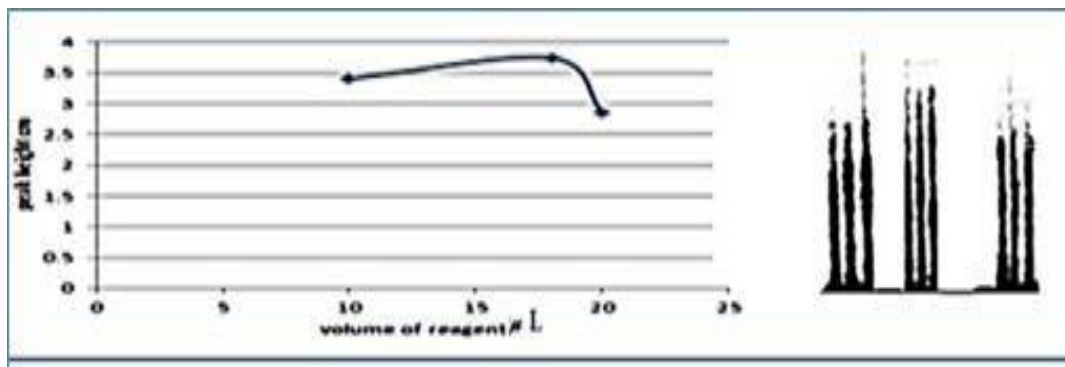

FIG. 5. **Change of peak height with reagent volume in FIA unit.**

TABLE 7. **Effect of reagent concentration on peak height at Zinc (II) ion conc.=10 mg/l, Reaction coil length)=50 cm, Dithizon conc.=5 × 10^{-5} mol/l, Sample volume=157.0 µl, Reagent volume=141.3 µl, SDS=0.01%, Flow rate=11.20 ml/min, in FIA unit.**

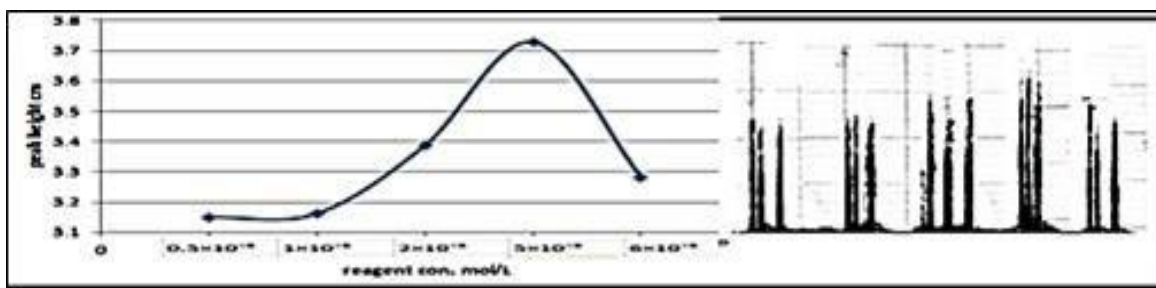| Conc. dithizone mol/l	Peak height Cm			Mean	SD	RSD%
0.5×10^{-5}	3.0970	3.0280	3.1200	3.0816	0.0469	1.5219
1×10^{-5}	3.1250	3.1340	3.2380	3.1623	0.0624	1.9732
2×10^{-5}	3.4410	3.4600	3.4600	3.4536	0.0070	0.2026
5×10^{-5}	3.7290	3.7020	3.7900	3.7290	0.1516	4.0531
6×10^{-5}	3.1610	3.1550	3.1300	3.1486	0.0141	0.4478

FIG. 6. **Change of peak height with reagent conc in FIA unit.**

Calibration curve in FIA

Attended chain from concentration ion between (0.01-50) mg/l at the optimum condition of complex ion and change in the ion concentration (TABLE 8, FIG. 7) that show curve is linear in the range of 2-10 mg/l.

TABLE 8. **Effect of the Zinc (II) ion concentration on peak height at Zinc (II) ion conc.=10 mg/l, Reaction coil length=50 cm, Dithizon conc.=5×10^{-5} mol/l, Sample volume=157.0 μl, Reagent volume=141.3 μl, SDS=0.01%, Flow rate=11.20 ml/min, in FIA unit, peak height of reagent=2.3892 cm in FIA unit.**

| Conc. of Zinc (II) ion mg/l	Peak height cm			Mean	Value after removed peak reagent	SD	RSD%
2	2.8570	2.8840	2.88366	2.8748	0.4856	0.0122	0.4243
3	3.1150	2.9000	2.9000	2.9716	0.5824	0.1238	4.1661
4	3.0230	3.0270	3.0303	3.0303	0.6411	0.0000	0.0000
5	3.1750	2.9620	3.2560	3.1310	0.7418	0.1516	4.0531
6	3.2700	3.2620	3.2593	3.2637	0.8745	0.0000	0.0000
7	3.3750	3.3 110	3.3220	3.3363	0.9468	0.0331	0.9922
8	3.3620	3.5960	3.6800	3.5400	1.1508	0.1647	4.6525
9	3.67300	3.5400	3.5580	3.5800	1.1908	0.0728	2.0335
10	3.7290	3.7020	3.7900	3.7030	1.3511	0.0441	1.1790
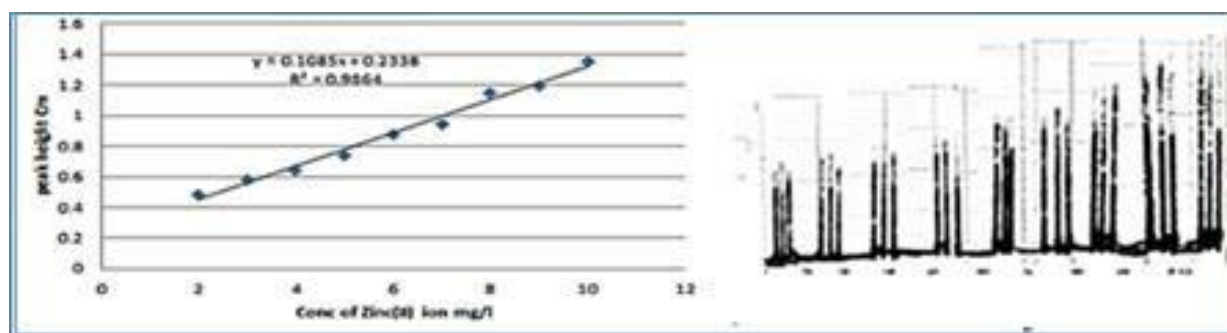
FIG. 7. **Calibration curve of Zinc (II) ion with dithizon in FIA unit.**

Repeatability

Repeatability was edifying through injection the same concentration of Zinc (II) ion complex. The concentration ion was 5 mg/L and 5×10^{-5} mol/l of dithizone (TABLE 9, FIG. 8) show the repeatability of Zinc (II) ion. The efficacy of the proposed FIA unit for the determination of Zinc (II) ion was reversed from the result of repeatability.

TABLE 9. **Repeatability for 10 mg/l of Zinc (II) ion in FIA at, Reaction coil length=50 cm, Dithizon conc.=5×10^{-5} mol/l, Sample volume=157.0 μl, Reagent volume=141.3 μl, SDS=0.01%, Flow rate=11.20 ml/min. in FIA unit.**

No of peak height	1	2	3	4	5	6	7	8	9	10	Mean	SD	RSD%
Peak height cm	3.729	3.702	3.729	3.790	3.702	3.729	3.790	3.702	3.729	*08709*	3.733	0.0317	0.8491

Calculation the modeling rate in the flow injection system

An experiment was carried out to calculate the number of analyzed sample in the hour after the best conditions were determined by calculating the time from injection to the maximum absorption value of the relevant concentration if it was found that the time required for the emergence of this absorption is 51 s and thus the modeling rate is 70 sample per hour.
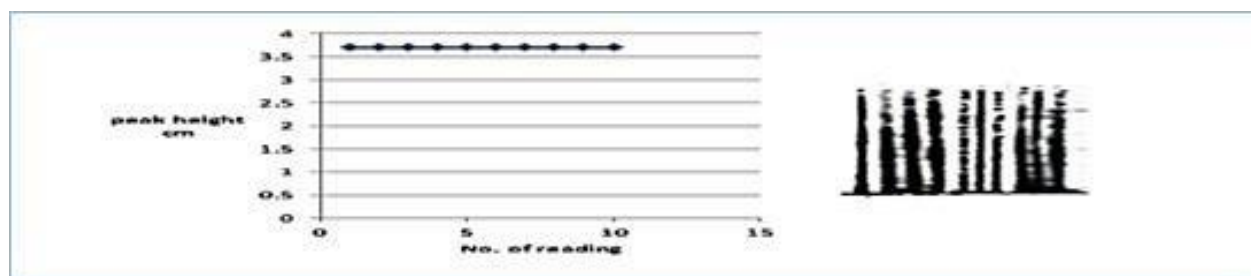

FIG. 8. **Repeatability for 10 mg/l with dithizone in FIA unit.**

Study of the interference of some ions in the flow injection system

In order to study the effect of the interferences, a number of negative and positive ions were taken to determine their effect on the process of estimating the dissolved in an alcoholic medium from micelle. The negative and positive ions studied were (Cl^-, CH_3COO^-, SO_4^{2-}, CO_2^-, F^-, Cd^2; Ca^2; Mn^2; Cu^2; Fe^2) and ions (TABLES 10 and 11). The experiment was carried out at concentrations of (5, 50) mg/L of the ion intermingled with 5 mg/l from ion Zinc (II) ion dissolve in alcoholic medium from an alcoholic medium of the micelle and concentration Reagent 5×10^{-5} mol/l. The results showed that the ions under study did not interfere with the Zinc (II) ion complex at the mentioned concentration.

TABLE 10. **Effect interferences negative on determination Zinc (II) ion.**

Change in the peak height m	Concentration of ion interference mg/l	Ion interference	Zinc (II) ion Concentration mg/l
0.7654	5	Cl^-	5
0.87643	50		
0.6672	5	SO_4^{2-}	
0.0981	50		5
0.6063	5	CH_3COO^-	5
0.8664	50		
0.2273	5	CO_3^{2-}	
0.3209	50		5
0.1991	5	F^-	5
0.9901	50		

TABLE 11. **Effect interferences positive on determination Zinc (II) ion.**

Change in the peak height cm	Concentration of ion interference mg/l	Ion interference	Zinc (II) ion concentration mg/l
0.8240	*0*	Cd^{2+}	5
0.8001	*03*		
0.6681	*0*	Ca^{2+}	
0.9987	*03*		5
0.0453	*0*	Mn^{2+}	5
0.9971	*03*		
0.5375	*0*	Cu^{2+}	5
0.01297	*03*		
0.7129	*0*	Fe^{2+}	
0.0072	*03*		5
0.2550	*0*	Ni^{2+}	5
0.8710	*03*		

Determination of dispersion

To measure the dispersion value in different sample zones of (10 and 5) mg/l Zinc (II) ion for FIA, two experiments were borne out. In the first experiment, after mixing of reactants (dithizone and Zinc (II) ion that passes through manifold unit gives continuous responsive and indicates non-existent of dispersion impact by convection or diffusion.

This measurement represents (H°). The experiment second includes injection different concentration of Zinc (II) ion (10 and 5) for FIA and signals recorded as H_{max}. The value dispersion (D) from this experiment can be calculated from this equation. $D = H°/H_{max}$. These values in limit state of dispersion (TABLE 12, FIG. 9).
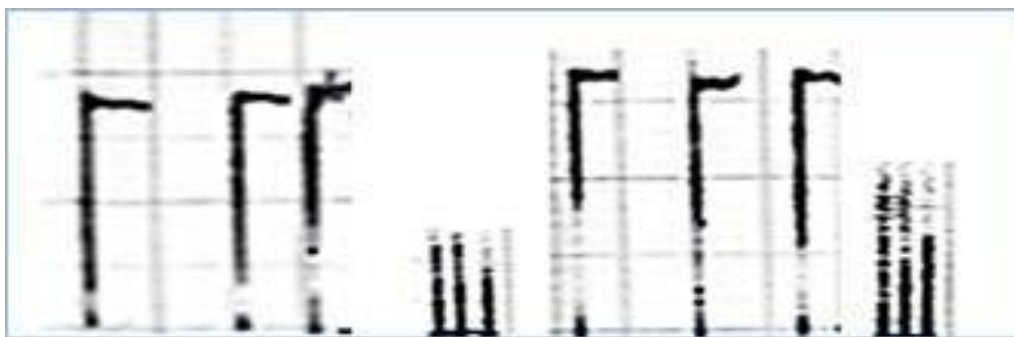

FIG 9. **Dispersion Zinc (II) ion in FIA system.**

SIA Unit

Effect of the flow rate

The effect of the flow rate on the peak height was the lesson in the range of 9-18 ml/min (TABLE 12, FIG. 10) show that. The flow rate was 13.00 ml/min as optimizing rate after that the height of peak was reduced due to declining the sensitivity of measurement in height flow rate because the reaction was no attained when increased the flow rate [21].

TABLE 12. **Effect of the flow rate on peak height at Zinc (II) ion conc.=5 mg/l, Reaction coil length=15 cm, Dithizon conc.=5 × 10⁻⁵ mol/l, Sample volume=157.0 µl, Reagent volume=141.3 µl, loading coil length=30 cm, SDS=0.01%, in SIA unit.**

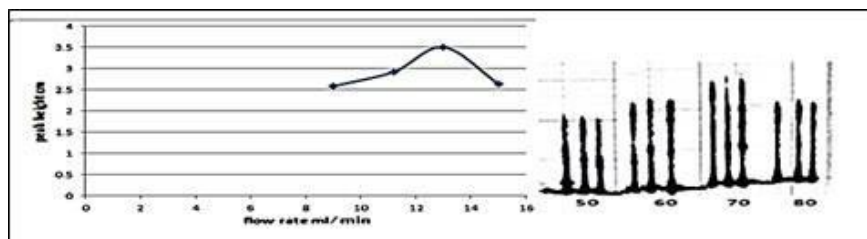| Flow rate ml/min	Peak height cm			Mean	SD	RSD%
9.00	2.6680	2.5740	2.5160	2.5860	0.064	2.9576
11.20	2.9260	2.9450	2.9010	2.9240	0.0212	0.7254
13.00	4.0010	4.1700	4.1000	4.0903	0.0842	2.0600
18833	2.6140	2.7000	2.6030	2.6390	0.0524	1.9856

FIG. 10. **Change of peak height with flow rate in SIA unit.**

Effect of loading coil in SIA

TABLE 13 and FIG. 11, has shown the effected of the loading coil Length on the peak height in the range 20-40 cm it was reading the suitable loading coil length was 30 cm, since it provided the larger sensitivity.

TABLE 13. **Effect of loading coil length on peak height at Zinc (II) ion conc.=5 mg/l, Reaction coil length)=15 cm, Dithizon conc.=5 × 10⁻⁵ mol /l, Sample volume=157.0 µl, Reagent volume=141.3 µl, SDS=0.01% in SIA unit.**

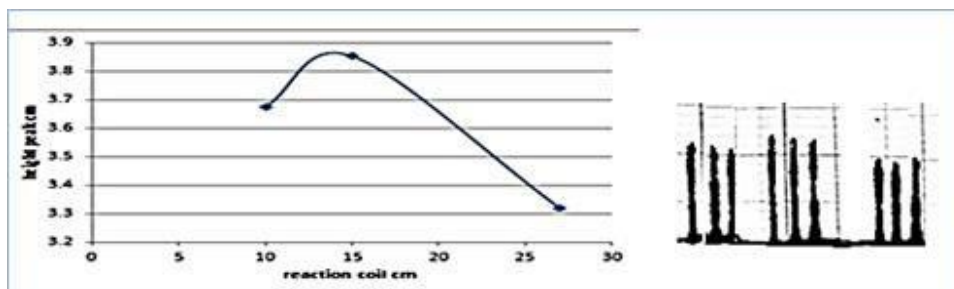| Reaction coil length cm	Peak height cm			Mean	SD	RSD%
03	3.5750	3.5860	3.5000	3.5536	0.0324	0.9118
03	4.0010	4.1700	4.1000	*083830*	0.0595	1.4566
40	3.6090	3.5750	3.6130	3.5990	0.0132	0.3675

FIG. 11. **Peak height with length of loading coil in SIA unit.**

Effect of the reaction coil length in SIA

TABLE 14, FIG. 12 have shown the effected of the reaction coil on the peak height in the range 10-20 cm it was reading the suitable reaction coil length was 15 cm since it provided the larger sensitivity.

TABLE 14. **Effect of on reaction coil length peak height at Zinc (II) conc.=5 mg/l, Dithizon conc.=5 × 10⁻⁵ mol/l, Sample volume=157.0 μl, loading coil length=30 cm, Reagent volume=141.3 μl, SDS=0.01%, Flow rate=13.00 ml/min. in SIA unit.**

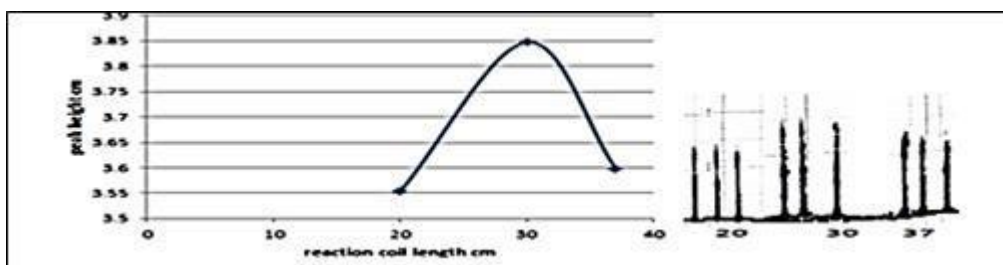| Reaction coil length cm	Peak height cm			Mean	SD	RSD%
10	3.6190	3.6800	3.6970	3.6653	0.0406	1.1076
15	4.001	4.1700	4.1000	*083830*	0.0842	2.0600
20	3.3657	3.2124	3.3670	3.3150	0.0509	1.5381

FIG. 12. **Change of peak height with reaction coil Length in SIA unit.**

Effect of the sample volume in SIA

The influence of the different volume 117.75 μl-235.5 μl of samples was observed sample volume that exhausted the greatest peak height was found to be 20 cm and it was chosen as the optimum (TABLE 15, FIG. 13).

TABLE 15. **Effect of the sample volume on peak height at Zinc (II) conc.=5 mg/l, Reaction coil length=15 cm, Dithizon conc=5 × 10⁻⁵ mol /l, Reagent volume=141.3 μl, Loading coil length=30 cm, SDS=0.01%, Flow rate=13.00 ml/min in SIA unit.**

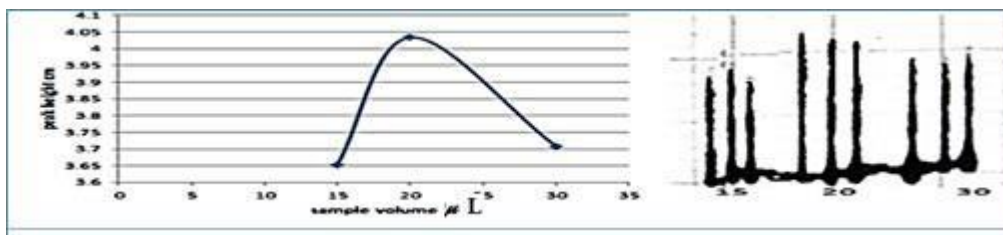| V of Zinc (II) ion μl	Peak height cm			Mean	SD	RSD%
*1*17.75	3.7050	3.6270	3.6280	3.6533	0.0435	1.1907
157.0	4.0010	4.1700	4.1000	4.0903	0.0842	2.0600
235.5	3.7610	3.7080	3.7080	3.7256	0.0300	0.8052

FIG. 13. **Change of peak height with sample volum in SIA unit.**

Effect of the reagent volume in SIA

The influence of the different volume 78.50 μl-157.0 μl of reagent was observed reagent volume that exhausted the greatest peak height was found to be 141.3 μl and it was chosen as the optimum (TABLE 16, FIG. 14).

TABLE 16. **Effect of reagent volume on peak height at Zinc (II) ion conc.=5 mg/l, Reaction coil length=15 cm, Dithizon conc.=5 × 10⁻⁵ mol/l, Loading coil length=30 cm, Sample volume=157.0 μl, SDS=0.01%, Flow rate=13.00 ml/min in SIA unit.**

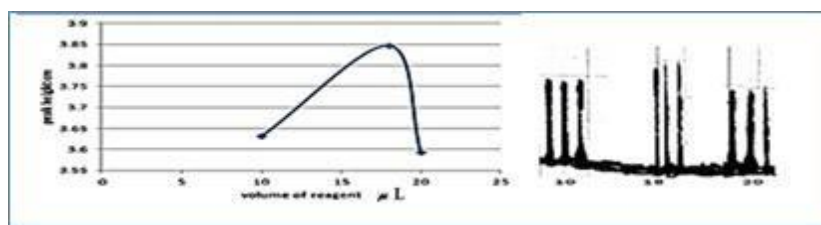| V of dithizone (II) μl	Peak height cm			Mean	SD	RSD%
78.50	3.6330	3.5960	3.6640	3.6310	0.0331	0.9115
141.3	4.0010	4.1700	4.1000	*083830*	0.0842	2.0600
157.0	3.5950	3.5900	3.5950	3.5933	0.0003	0.0000

FIG. 14. **Change of peak height with reagent volume in SIA unit.**

Effect of the reagent concentration

The same concentration of the reagent in the system FIA adopted in the system SIA, which give the best height and the best sensitivity is 5 × 10⁻⁵ mol/l.

Calibration curve in SIA

Attended chain from ion concentration between 0.5 mg/l-25 mg/l at the optimum condition of Zinc complex formation and change in the ion concentration (TABLE 17, FIG. 15), that show curve is linear in the range of 1 mg/l-15 mg/l.

TABLE 17. **Reaction coil length=15 cm, Dithizon conc.=5 × 10⁻⁵ mol/l, Sample volume=157.0 μl, Reagent volume=141.3 μl, SDS=0.01%, Flow rate=13.00 ml/min, Loading coil length=30 cm, Reaction coil length=30 cm peak height of reagent=2.9927 cm in SIA unit.**

Reaction coil length cm	Peak height cm			Mean	SD	RSD%
10	3.6190	3.6800	3.6970	3.6653	0.0406	1.1076
15	4.001	4.1700	4.1000	*083830*	0.0842	2.0600
20	3.3657	3.2124	3.3670	3.3150	0.0509	1.5381

Effect of the sample volume in SIA

The influence of the different volume 117.75-235.5 μl of samples was observed sample volume that exhausted the greatest peak height was found to be 20 cm and it was chosen as the optimum (TABLE 18, FIG. 16).
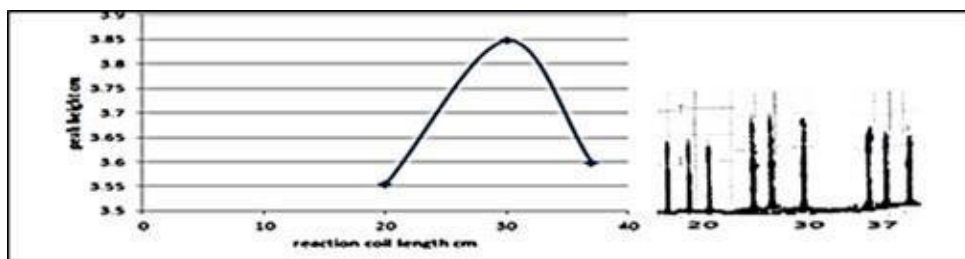
FIG. 15. **Change of peak height with reaction coil Length in SIA unit.**

TABLE 18. **Effect of the sample volume on peak height at Zinc (II) conc.=5 mg/l, Reaction coil length=15 cm, Dithizon Conc=5×10^{-5} mol/l, Reagent volume=141.3 μl, Loading coil length=30 cm, SDS=0.01%, Flow rate=13.00 ml/min in SIA unit.**

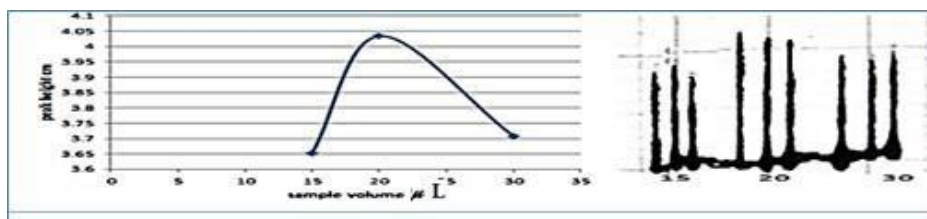| V of Zinc (II) ion μl	Peak height cm			Mean	SD	RSD%
*1*17.75	3.7050	3.6270	3.6280	3.6533	0.0435	1.1907
157.0	4.0010	4.1700	4.1000	4.0903	0.0842	2.0600
235.5	3.7610	3.7080	3.7080	3.7256	0.0300	0.8052

FIG. 16. **Change of peak height with sample volum in SIA unit.**

Effect of the reagent volume in SIA

The influence of the different volume 78.50-157.0 μl of reagent was observed reagent volume that exhausted the greatest peak height was found to be 141.3 μl and it was chosen as the optimum (TABLE 19, FIG. 17).

TABLE 19. **Effect of reagent volume on peak height at Zinc (II) ion conc.=5 mg/l, Reaction coil length=15 cm, Dithizon conc.=5×10^{-5} mol/l, Loading coil length=30 cm, Sample volume=157.0 μl, SDS=0.01%, Flow rate=13.00 ml/min in SIA unit.**

V of dithizone (II) μl	Peak height cm			Mean	SD	RSD%
78.50	3.6330	3.5960	3.6640	3.6310	0.0331	0.9115
141.3	4.0010	4.1700	4.1000	*083830*	0.0842	2.0600
157.0	3.5950	3.5900	3.5950	3.5933	0.000*3*	0.0000

Effect of the reagent concentration

The same concentration of the reagent in the system FIA adopted in the system SIA, which give the best height and the best sensitivity is 5×10^{-5} mol/l.
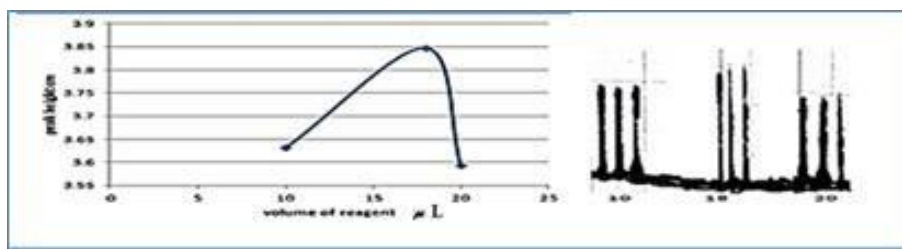
FIG. 17. **Change of peak height with reagent volume in SIA unit.**

Calibration curve in SIA

Attended chain from ion concentration between 0.5-25 mg/l at the optimum condition of Zinc complex formation and change in the ion concentration (TABLE 20, FIG. 18), that show curve is linear in the range of 1-15 mg/l.

TABLE 20. **Reaction coil length=15 cm, Dithizon conc.=5×10^{-5} mol/l, Sample volume=157.0 μl, Reagent volume=141.3 μl, SDS=0.01%, Flow rate=13.00 ml/min, Loading coil length=30 cm, Reaction coil length=30 cm. Peak height of reagent=2.9927 cm in SIA unit.**

| Conc. of Zinc (II) ion mg/l	Peak height Cm			Mean	Value after removed peak of reagent	SD	RSD%
1	3.3770	3.3670	3.1870	3.3103	0.3176	0.1067	3.2254
2	3.4560	3.4270	3.4100	3.4310	0.4383	0.0223	0.6499
3	3.7300	3.8100	3.8100	3.7900	0.7973	0.0469	1.2374
4	3.8800	3.9860	3.9870	3.9510	0.9588	0.0608	1.5395
5	4.0010	4.1700	4.1000	4.0903	1.0976	0.0842	2.0600
6	4.2925	4.2500	4.2501	4.2642	1.2715	0.0234	0.5499
7	4.3900	4.3990	4.3700	4.3863	1.3936	0.0122	0.2781
8	4.6400	4.6900	4.6700	4.6333	1.6406	0.0474	1.0237
9	4.8030	4.8300	4.8020	4.8100	1.8173	0.0141	0.2931
10	4.9000	4.9620	4.9350	4.9323	1.9396	0.0300	0.6082
10	6.0890	6.0001	6.0001	6.0303	3.0376	0.0360	0.5979
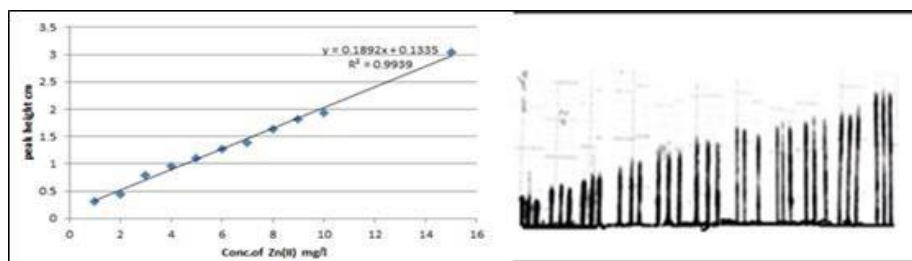
FIG. 18. **Calibration curve of Zinc (II) ion with dithizone in SIA unit.**

Repeatability

Repeatability was edified through re-injection the same concentration of Zinc (II) ion. The concentration ion was 10 mg/l and 1×10^{-5} mol/l from dithizone (TABLE 21, FIG. 19) show the repeatability of Zinc (II) ion. The efficacy of the proposed SIA units for the determination of Zinc (II) ion was reversed from the results of repeatability.

TABLE 21. **Effect of repeatability on peak height at Zinc (II) ion conc.=10 mg/l, Reaction coil length)=15 cm, Dithizone conc.=5 × 10⁻⁵ mol/l, Sample volume=157.0 μl, Loading coil length=30 cm, Reagent volume=141.3 μl, SDS=0.01%, Flow rate=13.00 ml/min in SIA unit.**

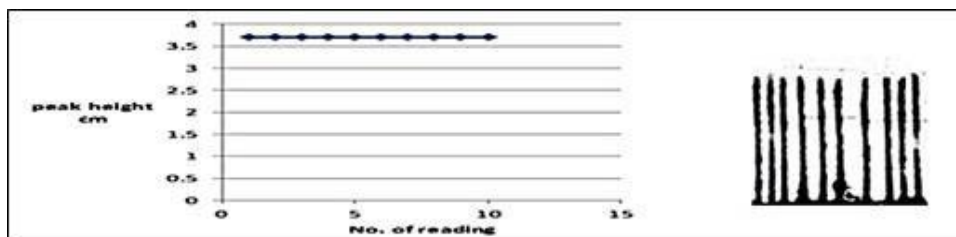| No of peak height	1	2	3	4	5	6	7	8	9	10	Mean	SD	RSD %
Peak height cm	4.935	4.900	4.962	4.935	4.900	4.962	4.935	4.900	4.962	4.935	4.932	0.0251	0.5089

FIG. 19. **Repeatability for 10 mg/l with dithizone in SIA system.**

Determination of dispersion

To measure the dispersion value in different sample zones of 10 and 5 mg/l Zinc (II) ion for SIA, two experiments were borne out. In the first experiment, after mixing of reactants (dithizone and Zinc (II) ion that passes through manifold unit gives continuous responsive and indicates non-existent of dispersion impact by convection or diffusion. this measurement represents ($H°$). the experiment second includes injection different concentration of Zinc (II) ions 10 and 5 for FIA and signals recorded as H_{max}. The value dispersion (D) from this experiment can be calculated from this equation. $D=H°/H_{max}$, These values in limit state of dispersion (TABLE 22, FIG. 20).

TABLE 22. **Dispersion value Zinc (II) ion conc=(5, 10), mg/l, ,Reaction coil length=15 cm, Dithizon conc.=5 × 10⁻⁵mol/l, Sample volume=157.0 μl, Reagent volume=141.3 μl, Loading coil length=30 cm, SDS=0.01%, Flow rate=13.00 ml/min in FIA system.**

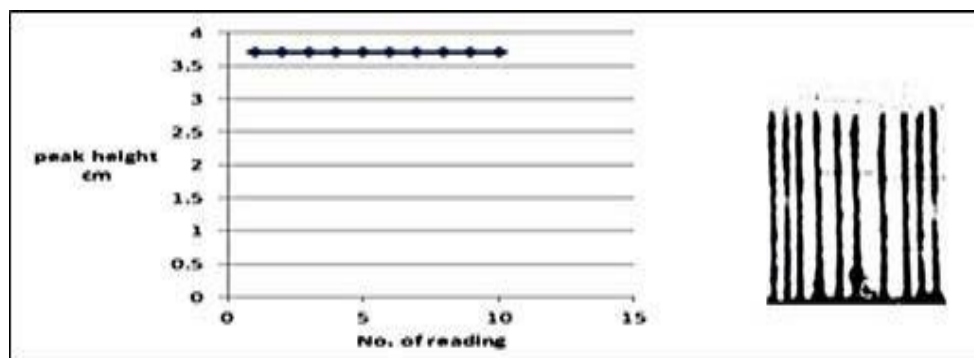| Conc. of ion Zinc (II) ion mg/l	Response cm		Dispersion (D) $D=H°/H_{max}$
	$H°$	H_{max}	
5	5.3118	4.0903	1.2986
10	6.1103	4.9323	1.2388

FIG. 20. **Dispersion in SIA unit.**

Effect of interfering ions

This effect of some actions (Cd^{2+}, Ca^{2+}, Mn^{2+}, Cu^{2+}, Fe^{2+}, Ni^{2+}) and anions (Cl^-, So_4^{2-}, CH_3COO^-, Co_3^{2-}, F^-) in determination of Zinc (II) ion it was 5 and 50 mg/l for each ions, and give the results noninterference between the Zinc (II) ion and ions interfering.

Application

The aim from this applied for the determination of Zinc (II) ion in pharmaceutical samples. The recoveries value is shown in TABLE 23.

TABLE 23. **Applied for the determination of Zinc (II) ion in pharmaceutical samples.**

Samples	Taken conc. of Zinc (II) ion using SIA system mg/l	Found value mg/l	Recovery %
Ostacare tablets vitabiotics lL td, 1Apsley Way London NW27HF, England.	5	5.8762	122.1426
Hemetic liquid mbH	5	5.9512	95.9362
Ferroveito liquid mbH	5	4.8543	97.0907
Ferromeria liquid mbH	5	6.01131	120.2262
Sample	Taken conc. of Zinc (II) ion using FIA system mg/l	Found value in mg/l	Recovery %
Ostacare tablets vitabiotics lL td, 1 Apsley Way London NW27HF, England.	5	5.3497	106.994
Hemetic liquid mbH	5	4.3292	86.584
Ferroveito liquid mbH	5	4.8115	96.2300
Ferromeria liquid mbH	5	4.7109	94.2180

Comparison between parameters of FIA and SIA unit

The results obtained from the methods used in the study were compared to the determination of the Zinc (II) ion (the injection method FIA and SIA) as shown in TABLE 24.

TABLE 24. **Comparison between some parameters of FIA and SIA units.**

Optical characteristics	FIA unit	SIA unit
Sample volume μl	157.0	157.0
Reagent volume μl	*1*41.3	141.3
Conc. reagent mg/l	5×10^{-5}	5×10^{-5}
Flow rate ml/min	13.000	11.20
Sample rate	70.000	64.000
Linearity range mg/l	2-10	1-15
Coefficient correlated	0.9864	0.9939
Slop	0.1085	0.1892
Detection limit mg/l practically	1.6746	0.1934
Relative standard deviation (%) determination for 10 mg/l n=10	0.8491	*380130*
Recovery %	86.584-106.994	95.9362-122.1426

Conclusion

It is concluded from this study that the Recovery % in SIA unit higher from recovery % in FIA unit, this means, SIA unit is more accurate than FIA unit for determination for Zinc (II) ion using dithizone.

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