Constructing and Building –up a home Made Semi-automated Ion Chromatography

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Abstract

Ion Chromatography (IC) is a chromatographic separation and measurement of ionic species. This technique combines an ion – exchange chromatographic separation with simultaneous conductometric detection for the determination of anions, cations and other ionic species.

Single – column IC system equipped with a conductivity detector and with a home-made flow cell 12.5 µl sample volume was constructed and build-up from simple and inexpensive parts readily available in our analytical laborites .The approach of single-column IC instrumentation depend on the small differences in the conductivity between sample ions and the prevailing eluent .To amplify these difference , low capacity exchanger are used for the home-made separation column (3 mm ID and 300 mm length) which permit elution with low electrolyte concentration .

The home-made single column IC has been applied to separate and determination of 25 µl of injecting, anions (F^- , Cl^- , Br^- , NO_2^- , NO_3^- , SO_4^{-2} and PO_4^{-2}) and cations (Li^+ , Na^+ , K^+ , NH_4^+) . The accuracy of the method was examined by performing a recovery experiments using standard additions method. The results were compared and good agreement was obtained (94.28- 100.58) %.

Keywords: Home-made ion chromatograph, single column, Anions, Cations.

Introduction

The origins of modern IC were laid down by Small et al. in 1975,   when they first described   a   novel   ion-exchange chromatographic method for the separation and   conductimetric   detection   of   ionic species(Small et al. 1975). They employed a low-capacity, ion-exchange stationary phase for   the   separation   of   analyte   ions,   in conjunction   with   a   second   ion-exchange

column and conductivity detector, which allowed for continuous monitoring of the eluted ions. The second column was called a suppressor and served the detectability of the eluted to reduce the background and served the detectability of the eluted to reduce the background conductance of the eluent and enhance ions (Small 2004).

Fritz et al. (1979) described an alternative separation and detection scheme for inorganic anions, in which the separator column is directly coupled to the conductivity cell. As a prerequisite for this chromatographic setup, low capacity ion-exchange resins must be employed, so that low ionic strength eluants can be used. In addition, the eluant ions should exhibit low equivalent conductances, thus enabling

Sensitive detection of the sample component (Weiss 2010).

Ion chromatography offers a number of advantages over other analytical methods in terms of speed, sensitivity, selectivity, simultaneous determination, stability and reliability of the method (Helaleh 2005). Since the sensitivity of conductivity detection does not suffer from   miniaturization, detection limits achieved for totally dissociated anions and low molecular weight organics compete well with those of ion Chromatography techniques (Cynthia 2007).

The aims of this work were to miniaturize a conductivity cell and building –up a home-made semi-au of ionic including (Li^+ , Na^+ ,

K^+ , F^- , Cl^- , Br^- , NO_2^- , NO_3^- , SO_4^{-2} and PO_4^{-3}) and evaluating the accuracy of this system.

To the best of our knowledge such as that IC system constructing and building –up a home- made semi-automated in this work have not previously been applied for separation and determination of ions in Basrah University

Experimental

All reagents used in this study were analytical grade unless otherwise stated and the stock and standard solutions were prepared in pure deionized water supplied from Al-Najibia power station (0.05 – 0.07 μS/cm   )and passed through 0.45 μm membrane filter before chromatographic analysis to avoid plugging the columns and to prevent damage of the flow system and the detector. All conductivity measurements were made at 25 $^\circ$C and the values of measurement as peak height were the reprint average of three successive measurements.

Reagents

Table 1 and Table 2 list the chemical compounds and the weight taken to preparer a liter of 1000 μg/L to each anions and cations respectively.

2 **Apparatus**

Figure(1) shows the home – made semi-automated IC system . In order to maintain a stable pulse free and easy to control the mobile phase flow rate (1.2 ml / min) a C/150 LKB with a dual piston   digitally

controlled pump was used . The sample was manually injected into the eluent by injection valve (Rheodyne, California) equipped with a variable sample loop in the range (25 – 200 cm) modified in local private workshop . The sample was pumping through a home- made separated column (300 mm , 3 mm i.d.) , which is packed with low capacity ion exchanger resin . The separated ions was measured using conductivity meter (Jenway PCM3) equipped with 12.5 μL volume home - made flow cell . The eulent reservoir and flow cell were immersed in beaker filled with water placed on regulator temperature hot plate (Lassco – India) and all conductivity measurement were made at 25 ºC . Siemens Kampensograph , 7KC , recorder was used to recorder the chromatogram .

Table (1) masses of compounds used to prepare

1 L of 1000 μg/L anion standard

Compound	Company	Purity	Anions	Mass (g)
NaF	B.D.H	98,7%	F^-	2.2090
NaCl	B.D.H	99%	Cl^-	1.6480
$NaNO_3$	Merch	98,9%	NO_3^-	1.3710
KH_2PO_4	Merch	98,7%	PO_4^{3-}	1.4030
Na_2SO_4	Merch	98,8%	SO_4^{2-}	1.1930
$NaNO_2$	Merch	98,8%	$NO2-$	1.5000

Preparation of the Separated Colums

　　The separator columns were prepared as follows (Simkin 2004). The ion exchange resine was rinse in deionize water for 48 h. The ion exchange was added slowly to 300 mm long (3 mm i.d.) glass tube until the required packing was achieved. A glass wool was put at both ends of the column to prevent movement of the fines broken beads of resin by the eluent and also to decrease physical plugging the column. A small piece of silicon rubber tubing (0.8 mm i.d.) was pushed into each end of the column so as to achieve a very tight connection. An electronic vibrator (Pifeo, 50 Hz) was used to settle the particle beads uniformly. Care must be taken to eliminate air pocket from the resin beads. The column was washed with deionized water until a steady baseline was obtained. The column was stored in this condition until required for use

Table (2) masses of compounds used to prepare 100mL of 10000 µg/mL cations standard.

Compound	Company	Purity	Cations	Weight (g)
LiCl	B.D.H	99%	Li^+	6.1070
NH_4Cl	B.D.H	99%	NH_4^+	2.9696
NaCl	R.D.H	98%	Na^+	2.5420
KCl	R.D.H	98%	K^+	1.9067
$CaCl_2$	B.D.H	99%	Ca^{2+}	2.7690
$MgCl_2$	Merck	99%	Mg^{2+}	3.9170
$BaCl_2$	Fluka	98%	Ba^{2+}	1.5160
$FeCl_3$	Merck	97,8%	Fe^{3+}	2.9040
$AlCl_3$	B.D.H	99%	Al^{3+}	4.9410

Procedure

A small volume of an aqueous sample typically (25 µL) is injected into an IC eulent to fill a constant volume sample loop. The sample is then injected into flowing stream of HCl or a mixture of $NaHCO_3$ and Na_2CO_3 for anions and cations respectively. The sample pumped through separated column packet with low capacity ion exchange resin and then into conductivity detector equipped with a home – made flow cell. The peaks height which is related to the identification and concentration of the separated ions based on the retention times and calibration curves generated from known standards .

Result and Discussion

Flow cell design

The most crucial and novel part in the IC system, which was developed and studied in the present work was the flow cell, especially designed for the IC applications. Figure (2) shows the home – made flow cell, free of dead volume with gold electrodes and cell constant 1.25 cm^{-1} . To achieve high standard performance of separation and determination of ions, a volume 12.5 µL conductivity cell has been designed and the conductivity measured at precisely control temperature (25 º C).
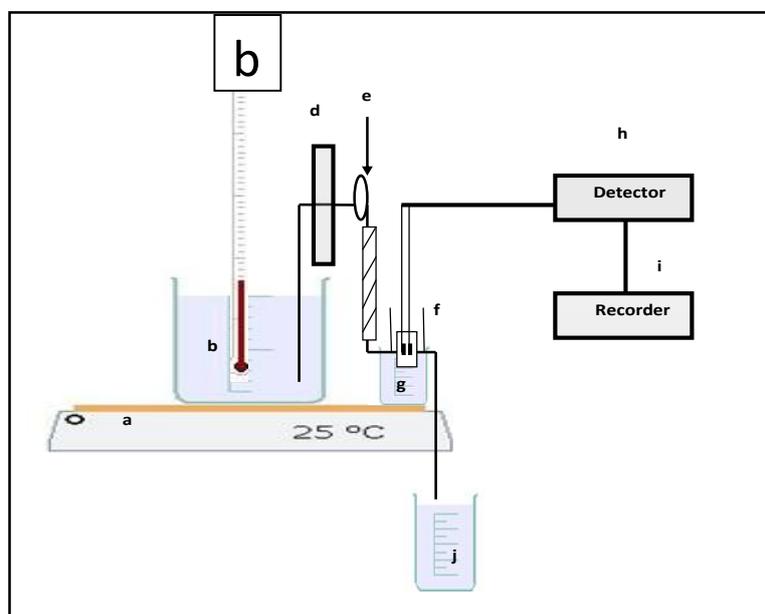
Figure(1) (a) Home-made semi-automated Ion Chromatography system .

(b) Schematic of an Ion chromatography system .

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a- Hot Plate
b- *Eluent*
c- Thermometer
d- Pump
e- Injection Valve
f- Flow Cell
g- Water Bath
h- Conductivity Meter
i- Recorder
j- Waste
k- Column

c
d
e
h

Detector

i

Recorder

b
g
f

25 °C

j

$$A \qquad = \frac{\ell}{a} =$$

$$\frac{0.1 \, \frac{cm}{cm^2}}{0.08} = 1.25 \; cm^{-1}$$

(+) electrode

Fluid In

0.1 cm

electrode (-)

Flow in Plannar Electrode

0.2cm

0.4 cm

0.08 cm²

Cell Volume
$(r_1)^2 \times \pi \times h$
r_1:radius
h:Cell Height
$(0.1cm)^2 \times 3.14 \times 0.4cm = 12.56 \, \mu l$

Teflon Tubing

Volum 2.5 µl

r_2

r_1
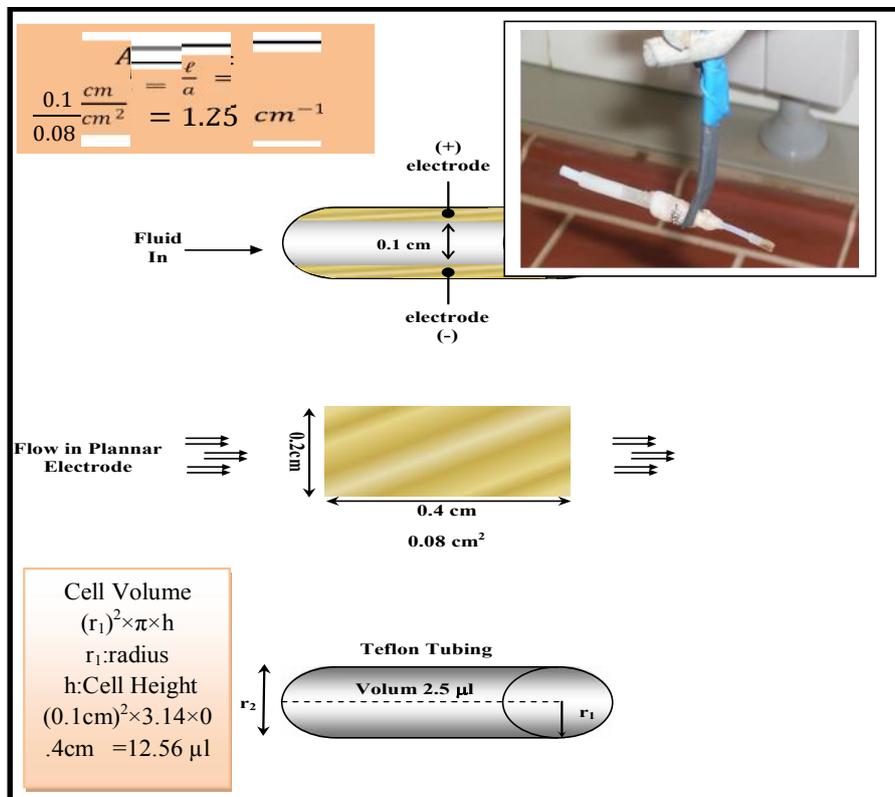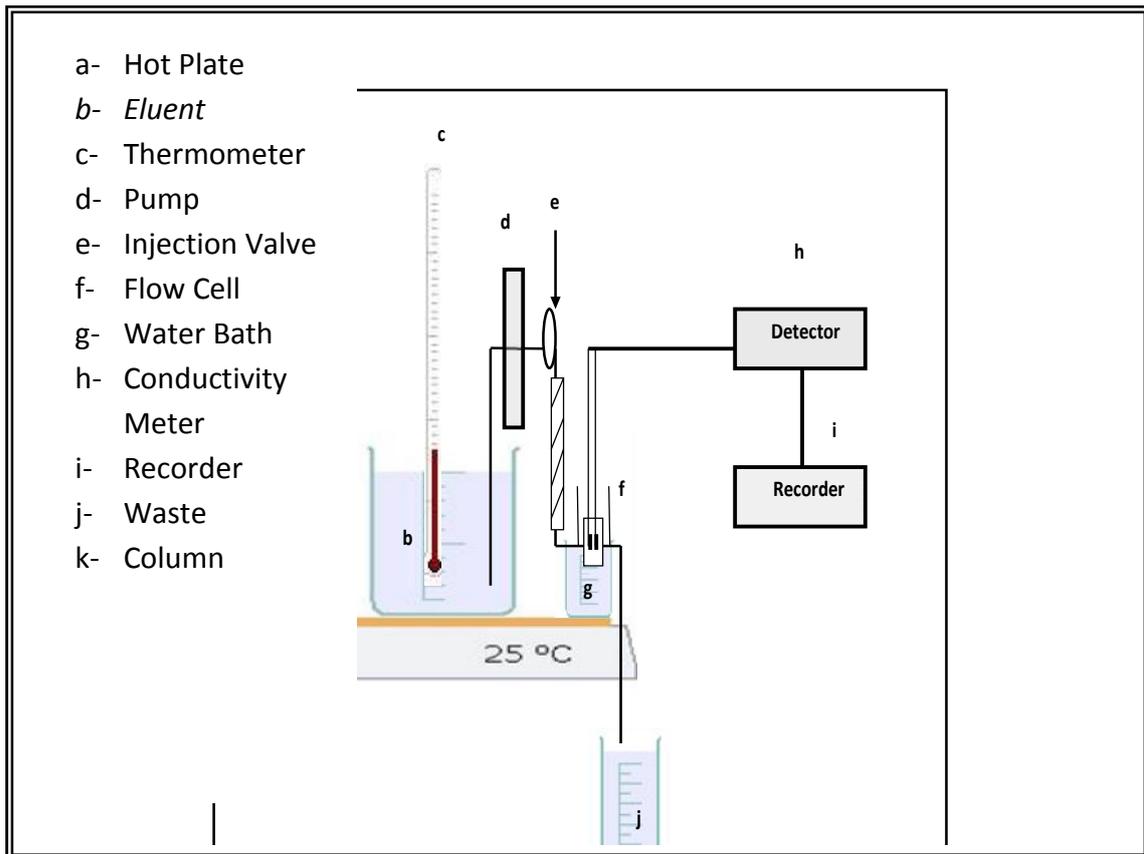
Fig.2 . Cell design and cell constant .

Determination of Retention Times

The Retention times (**R$_t$**) of cations and anions were determined to each ion by obtained separate chromatogram for each ion independently. This method, in spite of time consuming, but gives precisely Rt. Table (3) list the **R$_t$** for all ions.

Accuracy

To evaluated the accuracy of the home-made IC system. A recovery experiments were performed on water, drug and a representative samples by using standard additions method was used for all of these determination(Table 4) . The average

recoveries were in the range (92.72 – 102.8 %).

In order to establish the validity of the home-made IC system the same batch of representative samples (Table 4) were analysed by IC system and another methods such as flame photometery (Al-Mossaoy 2009) for Na$^+$ and K$^+$, gravimetric analysis (Christian 2006) for Cl$^-$ and truibimetry(APHA 1989) for SO$_4^{2+}$. Standard additions method was used to avoid all possible interferences. A good agreement between the results was obtained as shown in table 4 , which clearly indicated that home-made IC system can be used for several applications .

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Table (3) Retention times of some cations and anions

Ion	Retention Time (Min.)
Li$^+$	0.5
Na$^+$	4.5
K$^+$	10
NH$_4^+$	12
F$^-$	1.0
Cl$^-$	4.0
NO$_2^-$	4.3
NO$_3^-$	4.5
PO$_4^{-3}$	8.5
SO$_4^{-2}$	12

Table (4) Ions recoveries obtained by IC and other methods .

Ions	Claimed (µg/L)	Determination by IC		Determination by Other Methods	
		Found µg/L	Recovery % ±r.s.d%	Found µg/L	Recovery% ±r.s.d%
Na^+	7.9	7.6	96.20 ± 1.0	6.84	94 ± 0.9
K^+	3.5	3.3	94.28 ± 0.9	2.84	95.33 ± 0.86
Cl^-	6.2	6.0	96.77 ± 1.2	5.70	97 ± 0.98
SO_4^{2+}	51	51.3	100.58 ± 1.1	47.8	98.7 ± 1.68

Analytical Performance

Under the established conditions listed in Table 5 and Table 6 for separation and determination of cations and anions respectively. Linear calibration plots of peak height aginst concentrations of cations or anions were obtained, correlation coefficients and detection limit (S/ N = 2) were summarized in Table 7.

The reproducibility of peak heights and R_t the conditions listed in Table 8. Relative standard deviations (R.S.D. %) were calculated for six chromatographic runs for each ions . The values obtained were between (0.9 – 1.50 %) and (0.9 – 1.40 %) for peak heights and R_t respectively.

Table (5) The optimum conditions for separation and determination of anions

Parameters	Values
Distribution factor for selective resin (D)	1.36 for weak basic resin (A500-OH)
Conc. of Anion Mixture	50 µg/ml
Length column	30 cm (Length)× 3 mm (i.d)
Sample volume	25 µl
Type of eluent	$Na_2CO_3/NaHCO_3$ (1:1)
pH	7.5-10.5
Flow Rate	1ml/min
Volume of Flow cell	12.30 µl
Temperature	25^oC
Pressure	100 Psi
Sample through put	5 sample/h

Application

The home-made semi-automated IC system was used successfully to the separation and determination of many samples. The chromatogram presented in Fig.3 shows the separation of mono valiant ions, the peak resolution was quite satisfactory and easily to identify the separated cations from their retention times   (Alsalman 2012). The simultaneous determination of mono and divalent in natural water obtained by the home-made IC chromatography (fig.4). Figure also shows that monovalent cations were eluted earlier than divalent cations from column , this gave the impression that typical cation – exchange interaction was occurring.

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Table (6): The optimum conditions for separation and determination

of Mono, Di and Tri Cations

Parameters	Value Mono Cation	Value Di Cation	Value Tri Cation
Flow rate	1.2 ml/mint	1.2 ml/mint	1.2 ml/mint
Sample Volume	25 µl	25 µl	25 µl
Mixing Coil	5cm	5cm	5cm
Distribution factor for selective Resin (D)	14.3 for Weak acidic Resin (One Charge Ion)	2.42 for Strong acidic Resin	2.42 for Strong acidic Resin
Separation column Length	30 cm (Long) × 3 mm (I.d)	30 cm (Long) × 3 mm (I.d)	30 cm (Long) × 3 mm (I.d)
pH Eluent (HCl)and Weak Basic Solution(Na_2CO_3)	3.7-7.5	3.7- 4	3.7- 4
Flow Cell volume	12.30 µl	12.30µl	12.30µl
Temperature	25°C	25°C	25°C

Table (7): Data for the ions separated and determined by

the home-made IC system.

Ions	Linear range µg/mL	Correlation coefficient(r^2)	Detection limits (µg/mL)
Li^+	1.0 - 7000	0.9830	1.0
Na^+	1.0-6000	0.9710	1.0
K^+	1.0-9000	0.9969	1.0
Cl^-	1.0 - 100	0.9959	0.1
SO_4^-	1.0 – 50	0.9439	0.1

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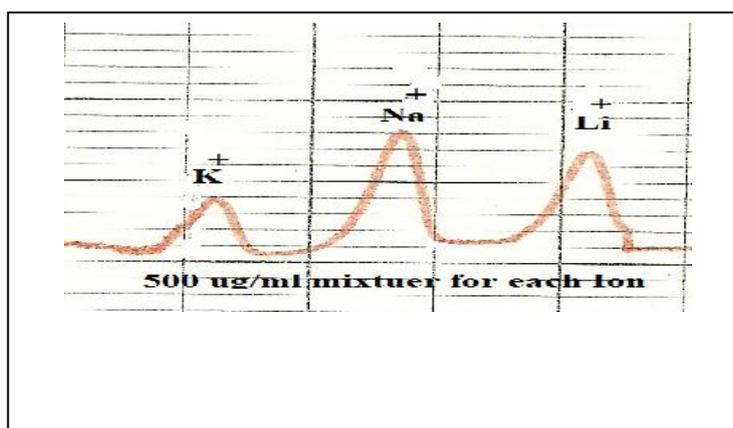
Figure (3)   Separation of mono cations by   home-made IC.

Table (8): Relative deviation of peak height and R_t for the ions separated

and determined by The home-made IC system

Ions (µg/mL)	Peak height R.S.D. %	R_t R.S.D. %
Li^+	1.50	0.90
Na^+	1.10	1.0
K^+	0.90	1.3
Cl^-	1.20	0.98
SO_4^-	1.10	1.40
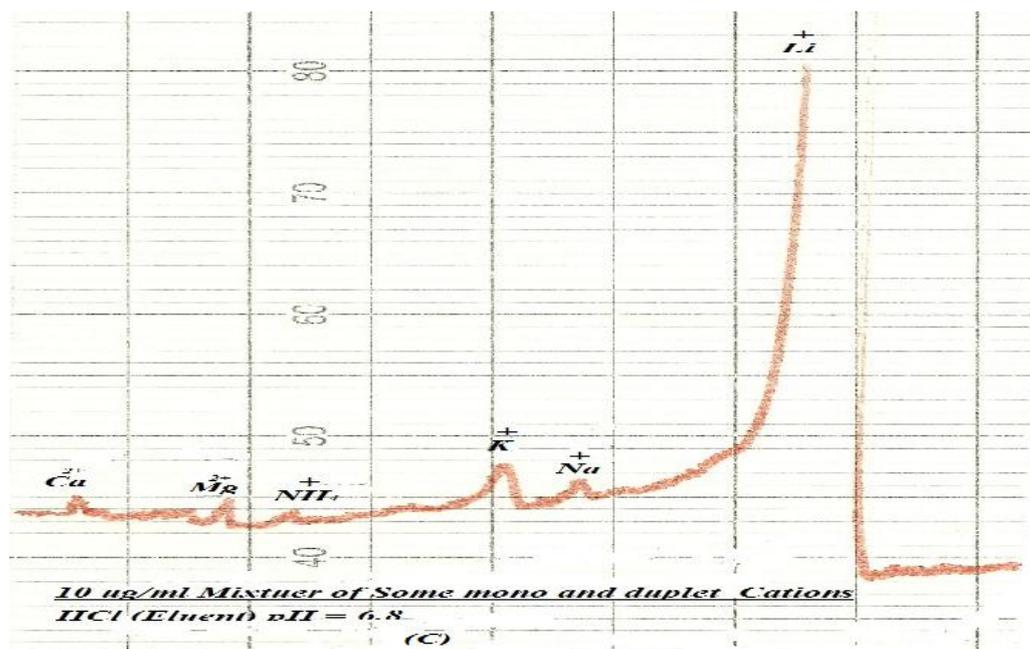
10 μg/ ml mixture of some mono and divalent cations

HCl (Eulent pH = 6.8

Figure (4)   Simultaneous IC of mono and divalent cations .

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Conclusion

Assembling a home-made semi-automated IC system from a few simple components and seeing it used to perform analysis with reproducibility and great rapidity was certainly satisfying experience.

IC chromatography is a technique which can supplement and in some application replace traditional classical methods of analysis .It permits simultaneous multi ion analysis in one sample injection. The home-made IC system offer many advantages of inexpensive, speed, wide linear range and requires only small volumes.

Reference

1. Al-Mossaoy Kh.R.K.H, M.Sc. Thesis, Basrah University (2009).

2. Alsalman H.N.K., M.Sc. Thesis, Basrah University (2012).

3. APHA (American Public Health Association), standard method for the examination water and waste water, 17th Ed. New York, U.S.A (1989).

4. Christian G. D., Analytical Chemistry, 6th ed. , John Wiley, New York , 2006

5. Cynthia G. Zoski ed., Handbook of Electrochemistry, Elsevier, Amsterdam, 2007.

6. Fritz J. S. and G. Senukler , Anal. Chem.,51,186 (1979) .

7 . Helaleh M.I.H. , Al-Omair A. ,Tanaka K. and Mori , Chromatographic Acta 15 (2005) 247 .

8.Small H. , T.S. Stevens, and W.C. Bauman , Anal. Chem. 47, (1975) 1801

9;Small H. , Ion chromatography, 81, 1277 (2004)

10. Simkin S. M . ,. Lewis D. N , Weathers K. C. ,. Lovett G. M and

Schwaez . K. , Water, air , and Soil pollution , 153 (2004) 343 .

11 .Weiss J. , Handbook of ion chromatography, 3rd ed. Chapter 2 , completely

revised and Enlarged, Wiley-VCH (2010) .

تصميم نظام كرومتغرافي محلي الصنع شبة ألي وبناءة

كامل حسين السوداني و حسين ناصر خلف الزيدان

قسم الكيمياء ـ كلية التربية ـ جامعة البصرة

الخلاصة

الكرومتغرافيا الأيونية هي فصل وتقدير الأيونات كالمشحونة. وتربط ما بين فصل الأيونات وتقديرها أنيأ باستعمال مقياس التوصلية لتقدير الأيونات السالبة والموجبة وكافة الأصناف المشحونة. صمم الكرومتغرافيا الأيوني أحادي العمود مع مقاس توصليه مجهز بخلية عابر، حجمها 12.5 µl مصممة محليا ، من الأجهزة والأدوات البسيطة و غير المكلفة والمتوفرة أصلا في المختبرات التحليلية .

تستند الكرومتغرافيا الأيوني احادي العمود على تضخيم الفرق البسيط بين توصيلية الأيونات المراد تقديره وتوصيلية المسيطرة للمزيج من خلال استعمال مبادلات أيونية مصممة محليا (نصف قطرها الداخلي 3 mm ID وطولها 300 mm) ذات سعات واطئة .

استعمل النظام المصمم في فصل ألأيونات السالبة (PO_4^{-2}, SO_4^{-2} , NO_3^- , NO_2^- , Br^- , Cl^- , F^-) والأيونات الموجبة (NH_4^+ , K^+ , Na^+ , Li^+) وتقديرها . فحصت دقة النظام بانجاز تجارب الأستعادية وباستعمال طريقة الإضافات القياسية و قورنت بالطرق الكلاسيكية وأظهرت توافق جيد بحدود (94.28- 100.58 %) .