Determination of Some Cations
Using A Home- made Ion Chromatography System
تقدير بعض الأيونات الموجبة بأستحدام نظام كرومتغرافي أيوني محلي الصنع

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الخلاصة

صمم نظام كرومتغرافيا احادي عمود الفصل ومقياس التوصلية مجهز بخلية جريان عابر صممت محلياً بحجم (12.5 µL) . أستخدمت أجزاء بسيطة و رخيصة ومتوفرة في مختبرات الكمياء التحليلية . ان مبدأ نظام الكرومتغرافي أحادي العمود يعتمد على الفرق البسيط بين توصلية العينة و الخلفية أيونات المزيج المستخدم . من أجل تضخيم هذا الفرق يعبأ عمود الفصل (نصف قطره 3 mm , وطوله 300 mm) بمبادل أيوني ذو سعة واطئة (Purolite R-COO ⁻) والتي يسمح بأستخدام تراكيز واطئة من المزيج الأكتروليتي .

استخدم النظام المصمم لفصل وتقدير بعض الأيونات الموجبة وعند درجة 25º C .

قيمت دقة النظام المصمم بأجراء تجارب الأستعادية وبأستخدام طريقة الأضافات القياسية وقورنت النتائج مع الطرق الكلاسكية المعتمدة وتم الحصول على نتائج مقبولة وجيدة (100.28 – 94.28) وبمعدل أنحراف قياسي لست كرومتغرامات متتالية لأرتفاع القمة لكل أيون وكانت بمدى (1.50 – 0.9) وزمن أحتفاظ (1.40 – 0.9) على التوالي .

Abstract

Single – column ion chromatography system equipped with conductivity detector and with a home-made 12.5 µl sample volume flow cell can be constructed and build-up from simple , inexpensive and off the shelf parts readily available in our analytical laborites .The approach of single-column IC instrumentation depend on the small differences in conductivity between sample ions and the prevailing eluent .To amplify these difference , low capacity exchanger (Purolite -Slightly acid cation R-COO) 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 cations (Li^+ , Na^+ , K^+ , NH_4^+ Ca^{2+} , Mg^{2+} , Al^{3+} and Fe^{3+}) at 25ºC temperature . The accuracy of the home –made IC instrument was examined by performing recovery experiments using standard additions method. The results were compared with other classical methods and good agreement was obtained (94.28- 100.58)% . Relative standard deviations (R.S.D. %) were calculated for six chromatogram runs for each ions . The values obtained were between (0.9 – 1.50 %)   and (0.9 – 1.40 %)   for peak heights and retention times respectively.

Introduction :-

The origins of modern IC were laid down by Hamish Small et al. in 1975, when they first described a novel ion-exchange chromatographic method for the separation and conductimetric detection of ionic species[1]. 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 delectability of the eluted to reduce the background conductance of the eluent and enhance ions[2].

In 1979, Fritz et al. [3]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 conductance, thus enabling
sensitive detection of the sample component [4].

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(5).
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(6).
So, the aims of this work were to miniaturize a conductivity cell
and building –up a home- made semiautomatic single column IC to achieve the separation and conductimetric detection of ionic including (Li^+ , Na^+ , K^+ , NH_4^+ , Ca^{+2} , Mg^{+2} , Al^{+3} and Fe^{+3}) and evaluating the accuracy of this home –made IC 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 unvirsity

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. Also, during analytical application all conductivity measurements were made at 25 $^{\circ}$C and the value of measurements as peaks height were the average of three successive measurements.
Reagents
Table 1 list the chemical compounds and the weight dissolved to preparer one liter of 1000 mg/L to each cations. Standards are stable for at least one month when stored at 4 °C.

Table 1 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

Apparatus:

Fig.1 shows the home – made semi-automated IC system . In order to maintain a stable pulse free and easy to control mobile phase pumping (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 variable sample loop in the range (25 – 200 cm) modified in local private workshop .

a- Hot Plate
b- Eluent
c- Thermom
   eter
d- Pump
e- Injection
   Valve
f- Flow Cell
g- Water
   Bath
h- Conductivi
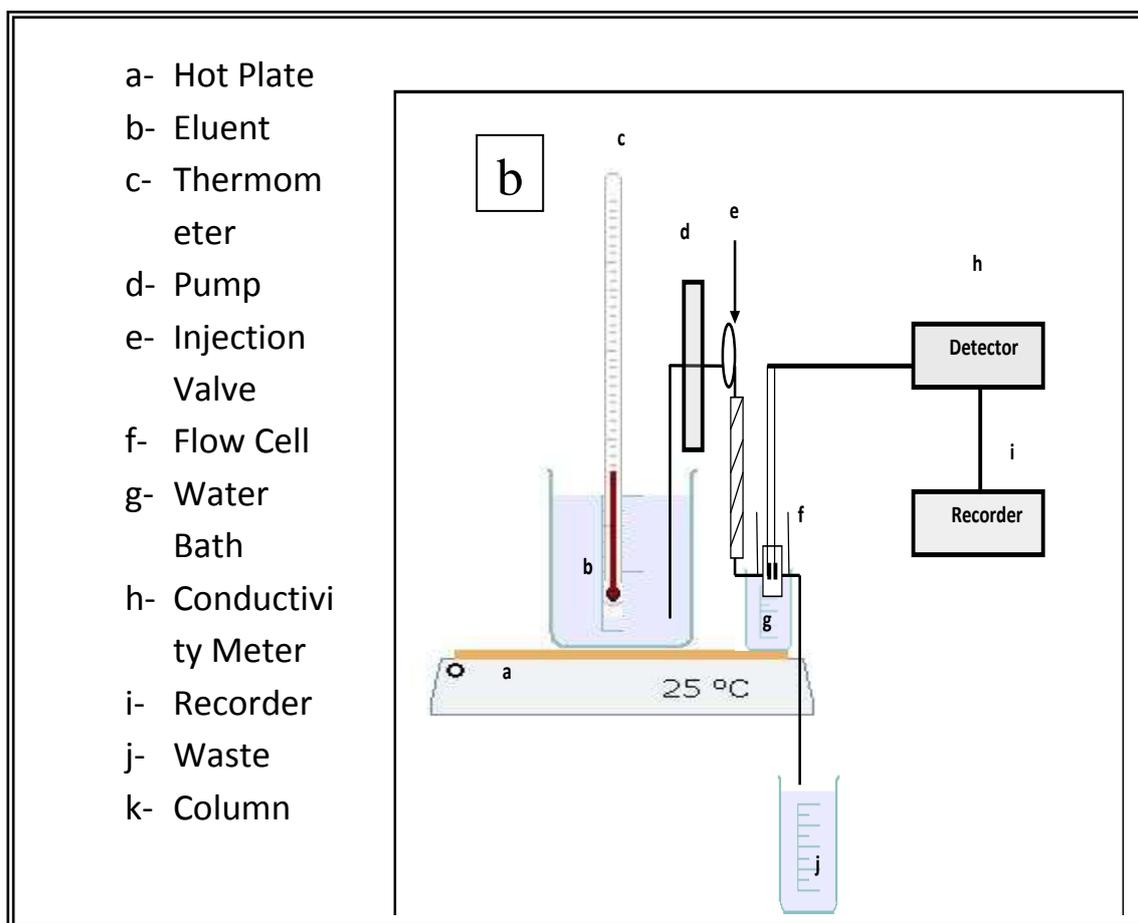   ty Meter
i- Recorder
j- Waste
k- Column

Fig. 1 .(a) Home-made semi-automated Ion Chromatography system .
      (b) Schematic of an Ion chromatography system .

The sample was pumping through a home- made separated column (300 mm long and 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 .

Preparation of the Separated Colum

The separator columns were prepared as follows (7) . The ion exchange was rinse in deionizer 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 thin layer (1.0 mm) of glass wool was put at both ends of the column to prevent movement of the fines broken beads of resine 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 particles plead uniformly. Care must be taken to eliminate air pocket from the resin beads . The column was washed with in pure deionized water until a steady baseline was obtained . The column was stored in this condition until required for use .

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 can be related to identification and concentration of the separated ions based on the retention times and calibration curves generated from known standards , respectively .

Result And Discussion

Flow cell design :-

The most crucial and novel elements in the IC system , which was developed and studied in the present work was the flow cell , especially designed for the IC application .

Figure (2) shows the home – made flow cell, free of dead volume with gold electrodes and 1.25 cm^{-1} cell constant . To achieve high standard of performance of separation and determination of ions , very low volume 12.5 µL , conductivity cell has been designed and is precisely control temperature (25 º C) .
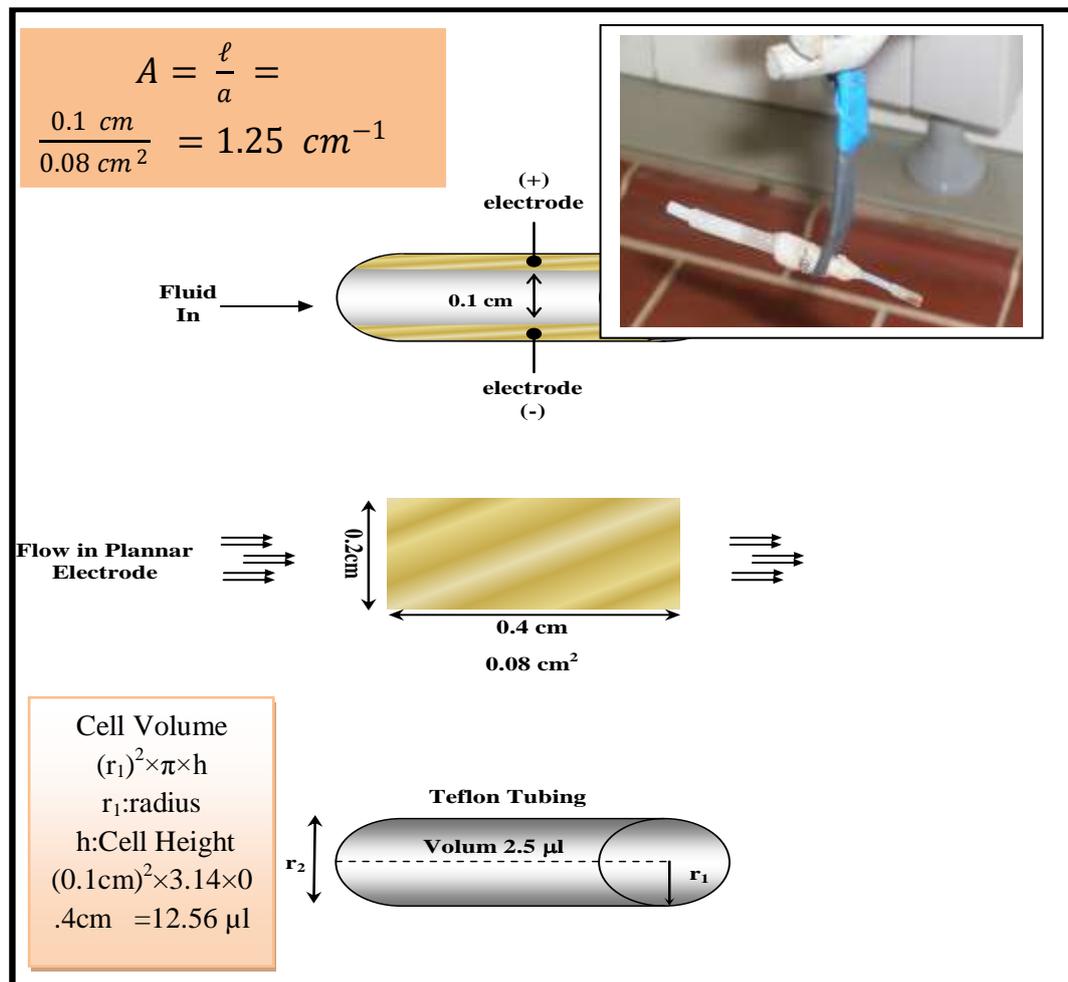
$$A = \frac{\ell}{a} = \frac{0.1\ cm}{0.08\ cm^2} = 1.25\ cm^{-1}$$

(+) electrode

Fluid In

0.1 cm

electrode (-)

Flow in Plannar Electrode

0.2cm

0.4 cm

0.08 cm^2

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 μl

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 independently . This method, in spite of time consuming , but gives precisely R_t .   Table (2) for all ions separated and determined in this study .

Table 2 Retention time of some cations

Ion	Retention Time (Min.)
Li^+	0.5
Na^+	4.5
K^+	10
NH_4^+	12

Accuracy :-

To evaluated the accuracy of the home-made IC system . A recovery experiments were performed on water , drug and representative samples . Addition standard methods were used for all of these determination (Table 4) summarize all of these studies . 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 3) were analysed byflame photometery (8)

methods also been used for evaluating the values obtained by IC system . An addition standard methods were used to avoid all the possible interferences . A good agreements between the results was obtained as seen in table 3 , which clearly indicated that home-made IC system can be used for several applications .

Table 3 . Ions recoveries obtained by IC and other methods .

Ions	Claimed (µg/L)	Determination by IC		Determination by flame photometery	
		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 ± 0.92
K^+	3.5	3.3	94.28 ± 0.9	2.84	95.33 ± 0.86

Analytical Performance

Under the established conditions listed in Table 4 the cations were separated and determined..Linear calibration plots of peak height against concentration were obtained , correlation coefficients and detection limits   (S/ N = 3) were summarized in Table5 .

Table 4 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 Resein (D)	14.3 for Weak acidic Resein(One Charge Ion)	2.42 for Strong acidic Resein	2.42 for Strong acidic Resein
Separation column Length	30 cm (Long) $\times$ 3 mm (I.d)	30 cm (Long) $\times$ 3 mm (I.d)	30 cm (Long) $\times$ 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^oC	25^oC	25^oC

Table 5. Calibration data for the ions separated and determined by
The home-made IC system .

Ions	Linear range µg/mL	Correlation coefficient (r^2)	Detection limits (S/N =3 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

The reproducibility of peak heights and R_t the conditions listed in Table 6 . 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 6 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

Application :-

The a home-made semi-automated IC system was used successfully applied to separation and determination of many samples   . The chromatogram is which presented in Fig.3   shows the separation of mono valent ions , the peak resolution was quite satisfactory and easily to identify the separated cations from their retention times . cations from column , this gave the impression that typical cation – exchange interaction was occurring (9).
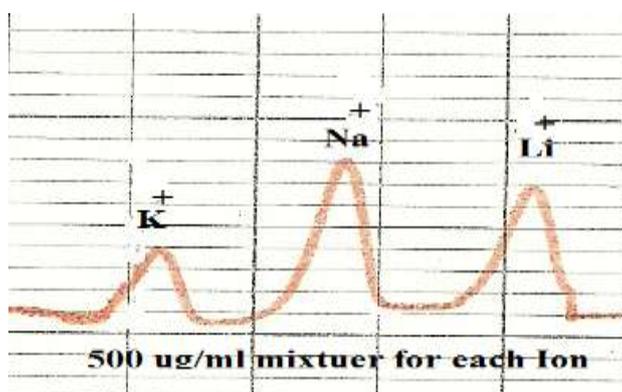

Figure 3 . Separation of mono cations by home-made IC
Chromatography .

The simultaneous determination of mono and di cations in natural water obtained by the home-made IC chromatography (fig.4) . Figure 4 also shows that monovalent cations were eluted earlier than divalent
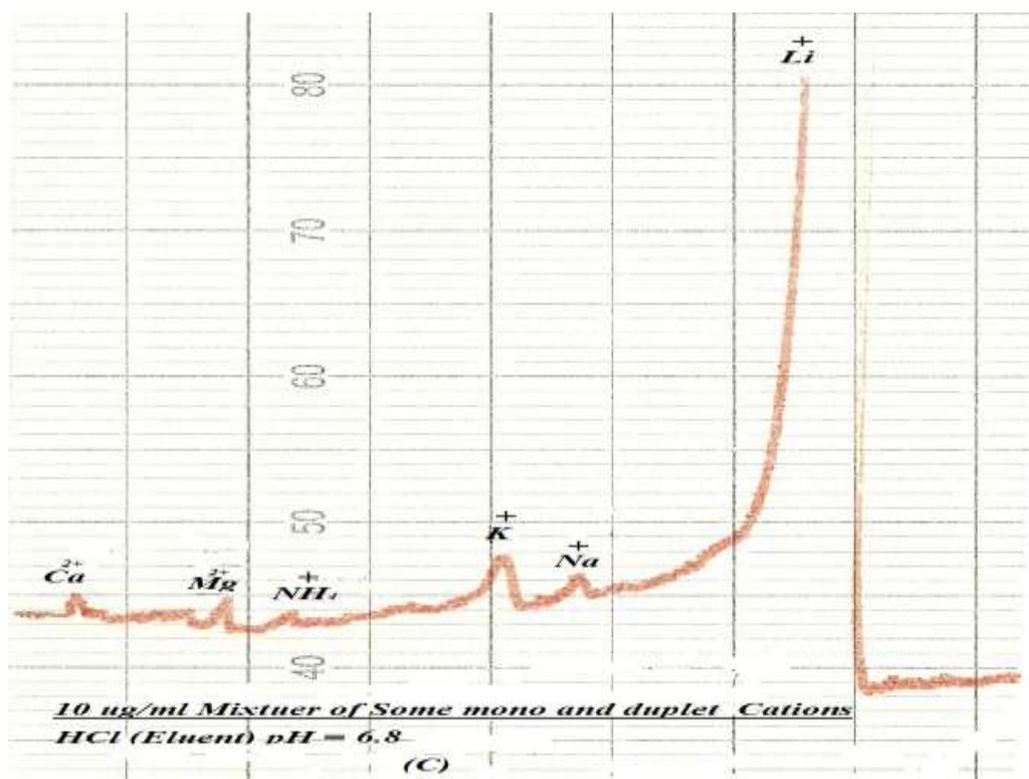
Figure 4   Simultaneous IC of mono and di cations .

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 on one sample injection . The home-made IC system offer many advantages of inexpensive , speed , wide linear range and requires only small volumes .

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