

Simultaneous Determination of Anions and Cations by Home – made Ion Chromatography System

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Abstract: -

A simultaneous method for analysis of anions and cations with home - made ion chromatography. Sulfosalicylic acid and 18 - crow - 6 - ether were used as mixed eluents for separations with conductivity detector. Ion chromatography column was prepared by mixed weak acid resin with weak base resin with equal ratio. The optimum conditions were optimized and linearity was fined in the range (5 – 150 $\mu\text{g/ml}$) and (1 – 140 $\mu\text{g/ml}$) for anions and cations respectively. Detection limit was in the range (0.5 – 0.075 $\mu\text{g/ml}$) and (0.15 – 0.25 $\mu\text{g/ml}$) for cations and anions respectively, with relative standard deviation in the range (0.166 – 0.250 %) and (0.45 – 0.90 %) for peak height to anions and cations respectively. This method applied to determine anions and cations in water samples and pharmaceutical preparations.

Introduction

Ion chromatography is one member of chromatography which subdivide to three types : Ion exchange chromatography is simply refer as ion chromatography, while ion pair chromatography and ion exclusion chromatography are regarded as being more specialize applications(Bhattacharyya and Rohrer) . Additionally a conductometric detector can be used as universal detector for the detection of both anions and cations (Jones, Knee, Small, Ming, and Weiss). Anions are detected directly and appear as increases conductance compared to the background, where cations are detected indirectly and appear as decreases in conductance compared to background, due to deficiency of alternative analytical procedures for trace anion analysis (Ohta *et al.*, Tanaka, Tanaka *et al.* and Tazuhiko *et al.*) The stationary phase was a weakly acidic cation-exchange resin mixed with a weakly basic anion-exchange resin with the same weight.

Sulfosalicylic acid, which is both strongly acidic and hydrophobic in nature, was used in this investigation for separation of inorganic anions. Sulfosalicylic acid contains three functional group when diluted, two of these (sulfonic and carboxylic) are dissociated and surrounded by negative charges and so it is hydrophobic absorption and influence on the retention time of acids can be neglected (Gentle *et al.* and Twohill).

Crown ether is well known as the highly selective separation agents (Panowo *et al.*) The ability of this macrocycle to form stable complexes with metal ions especially alkali and alkaline earth has lead to a wide range of analytical application (Kim *et al.*).

When used mixture from both Sulfosalicylic acid and 18 – crown-6-ether as an eluent, good resolution and separation for anions and cations was obtained.

The purpose of this work is to show that home – made ion chromatography system with conductometric detector which constructed and build up in our laboratory can be successfully used and will provide a mean for simultaneous a nalysis for several Inorganic anions and cations in different water samples.

Experimental

Sampling and Storage

The drinking, tab and rain water samples were collected in clean polyethylene vessels. Mineral waters were purchased from local markets. Analysis should be carried out as soon as possible after collection of the samples (APHA). All water samples were passing through 0.45 μm membrane filter (Millipore –USA) and keep frozen.

Reagents

During analytical application with home-made IC system, deionized water ($0.5 \mu\text{S}^{-1}$) supplied from deionized water unit in chemistry department, Education College for Pure Sciences, University of Basra, which was used throughout this work.

All chemicals were analytical grad, unless otherwise specified. The standard concentrations of nitrate, nitrite, bromide, sodium, ammonium and potassium, were prepared according to published procedure (Edwards *et al.*). The working and standard solutions were prepared by stepwise dilution by deionized water.

For simultaneous separation of anions and cations, the eluent was prepared by diluting 100 mM sulfosalicylic acid and 100 mM crown ether prepared by dissolving the

required weight of sulfosalicylic acid and 18-crown-ether (1, 4, 7, 10, 13, 16-hexaoxacyclooctadecane) in deionized water (Tanaka *et al.*). For the preparation of standard solutions of the desired anions and cations, commercially available analytical-reagent grade chemicals were used.

Instrumentation

All anions and cations were determined by using a semi-automated UV-IC system, as shown in figure (1). The constructing system, which is adapted to determine anions and cations are kept to be as simple as possible, there

fore a single manifold system was used. In order to maintain a stable pulse free and easily to control the carrier stream flow rate LKB pump was used to deliver the carrier stream with 1 ml min^{-1} . The sample injections were carried out through a microinjection valve (Pharmacia Fine Chemicals) with a sample loop of $25 \mu\text{L}$. Teflon tubing (0.8 mm i.d.) was used for the rest of the manifold. The Column was prepared as previously described (Tanaka and Fritz, Pakada) and operated at 25 C° with conductivity detector (Janway) equipped with $12.5 \mu\text{L}$ home-made conductivity cell. Siemens Kampensograph 7KC recorder was used to recorder the peak height which can be related to the concentration of the injected sample.

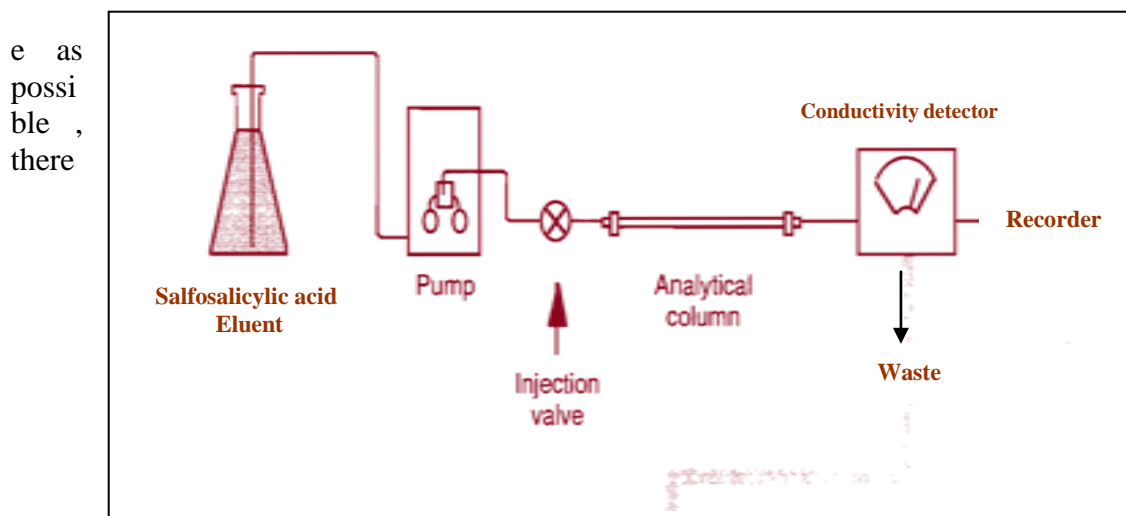


Fig.1 Semi-automated home-made IC – conductometric system

Procedure

The carrier stream (eluent) was 1.5 mM sulfosalicylic acid run into the manifold (Fig.1) at flow rate 1.25 ml min^{-1} . A $25 \mu\text{L}$ as a sample volume of anions and cations was injected manually through the injection valve into carrier stream. The sample

pumping through the home-made mixed bed ion-exchange column containing both cation and anion exchangers to conductivity detector equipped with $12.5 \mu\text{L}$ flow cell. The peak height of sample was recorded for each ion and its height can be related to the concentration of each ions.

Results and Discussion

In order to obtain the best analytical performance chromatographic operating parameter of this method, a series of experiments were conducted to establish the optimum parameters.

When the manifold system in figure 1 was used the peak height increased almost parabolically with increasing the injected volume between (25 - 100 μ l). The suitable maximum peak height was obtained when 25 μ l was injected. The effect of the flow rate on the peak height in the range 0.5 – 3.0 ml/min under the optimum conditions established previously, of 50 μ g /ml nitrite ion (NO_2^-). The peak height decreasing with increased flow rate. The effect of the column length in the ranged (100- 300 mm) on the peak obtained from injection 50 μ g/ml nitrite ion. The 100 mm column length with (3 mm id) was choice in the further

work due to high peak height 21 mm with 5 min retention time.

The effect of the pH on the peak height in the range (1.5 – 4) was studied. It is found that pH = 2.5 give the best result , this thought due to the basic environmental which lead to good separation and determination of NO_2^- and good reproducibility and height peak. Many types of eluent were studies for separation of nitrite ion with 50 μ g /ml concentration , 300 mm column length and show that the best eluent to separation was 80 mM sulfosalicylic acid. Table 1 listed the optimum conditions to studies.

Table 1. Optimum conditions used to determine ions with Conductivity – IC system

Parameters	Values
Column length	Home – made column 300 mm length x 3 mm id
Sample volume	25 μ L
Type of eluent	Sulfosalicylic acid(1.5mM)
pH	2.5
Flow rate	1.0 ml/min
Volume of flow cell	12.30 μ L
Sample throughput	12 sample / h

Separation of anions by conductivity - IC system

Under the optimum conditions which listed in Table 1 the mixture for $50 \mu\text{g ml}^{-1}$ concentration of three ions NO_2^- , Br^- , and NO_3^- were separated and determined with home – made conductivity - IC system.

The Rt of three ions NO_2^- , Br^- , and NO_3^- were determined, which show that $R_t = 5, 6, 6.5 \text{ min}$ for NO_2^- , Br^- ,

and NO_3^- ions respectively. The mixture of the three ions was separated with good resolution as seen in Figure 2.

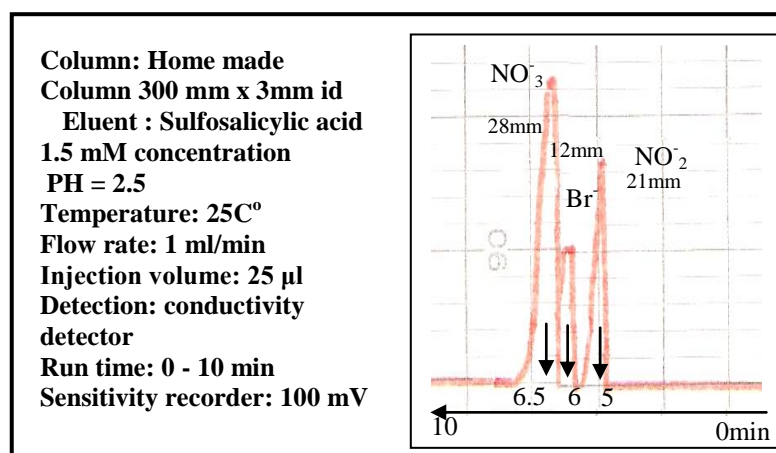


Fig.2 Separation of three anions NO_2^- , Br^- , and NO_3^- by Conductivity – IC system

Effect of the concentration of sulfosalicylic acid in the mobile phase

The effect of the concentration of sulfosalicylic acid in the mobile phase on the retention time R_t of the anions was investigated to optimize the separation conditions. Different concentration of sulfosalicylic acid from 0.5 to 2 mM was studied to determine the optimum concentration. Retention time values of the anions decreased as the concentration of sulfosalicylic acid in the mobile phase was increased as show in figure 3.

Relationships between the peak height and R_t of the anions and sulfosalicylic acid concentration are shown in Figure 4. Sulfosalicylic acid concentrations from 0.5 to 2.0 mM (R_t) values remain almost constant; 1.5 mM sulfosalicylic acid was therefore used throughout the research. Figure 5 show the Separation of three anions and three cations by using sulfosalicylic acid as eluente.

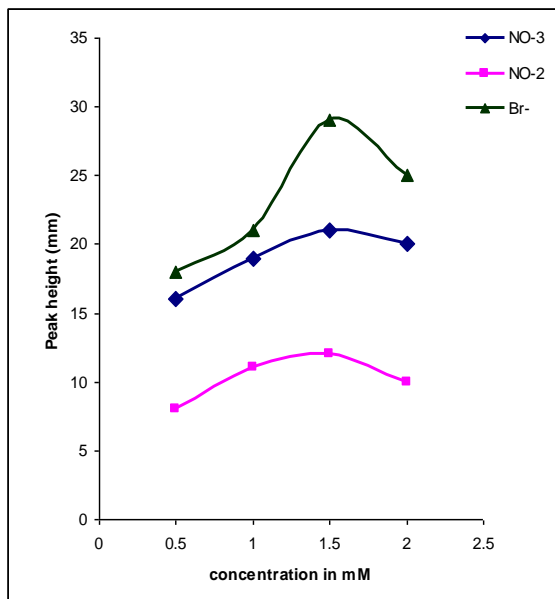


Fig.3 Effect of Sulfosalicylic acid concentration On the peak height of anions

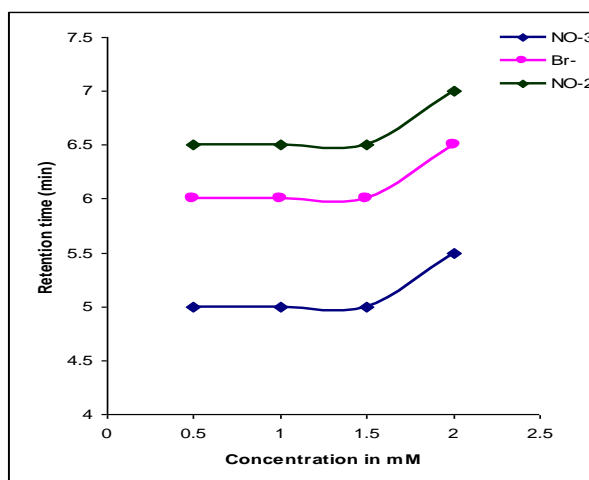


Fig.4 Effect of Sulfosalicylic acid concentration on the retention time of anions

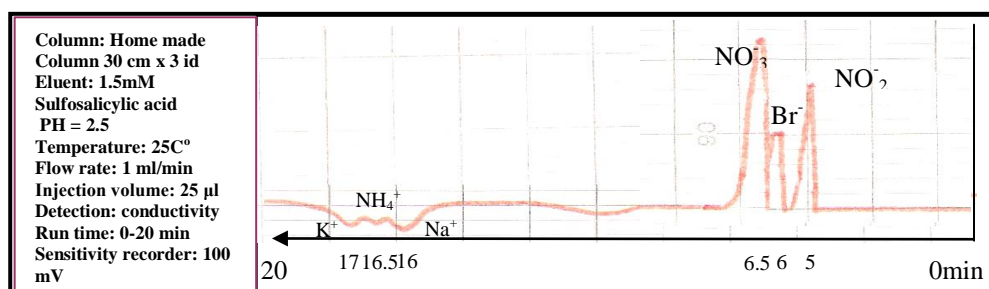


Fig.5 Separation of three anions and three cations by using sulfosalicylic acid as eluente

Calibration graph for separation anions

Under the established condition, a calibration graph for anions was obtained as shown in Fig.6. As observations the peak height increased with concentration of standard solution of anions increased. The linearity in the range 5 - 70 $\mu\text{g ml}^{-1}$, 5 - 80 $\mu\text{g ml}^{-1}$, and 10 - 150 $\mu\text{g ml}^{-1}$ for nitrite ion, nitrate ion, and bromide ion respectively, The relative standard deviation for six replicate analyses of 50 $\mu\text{g ml}^{-1}$ mixture of anions was 0.90 .The detection limited (3xNoise) 1 $\mu\text{g ml}^{-1}$ with retention time 1 – 8 min and sampling rate throughput for mixture of anions was 21 samples / h.

Analytical performance for separation anions

By using the Home – made ion chromatography system which operated at the optimum condition which established in the study. A linear calibration plotted of the average of triplicates peak height versus concentration for the three ions were obtained as show in table 2.

Separation of cations by conductivity-IC system

The optimum conditions listed in Table 1which were used to analysis the cations (Na^+ , NH_4^+ , and K^+) with conductivity - IC system.. Fig.7 shows the separation of 50 $\mu\text{g mL}^{-1}$ concentrations of Na^+ , NH_4^+ , and K^+ and the retention times.

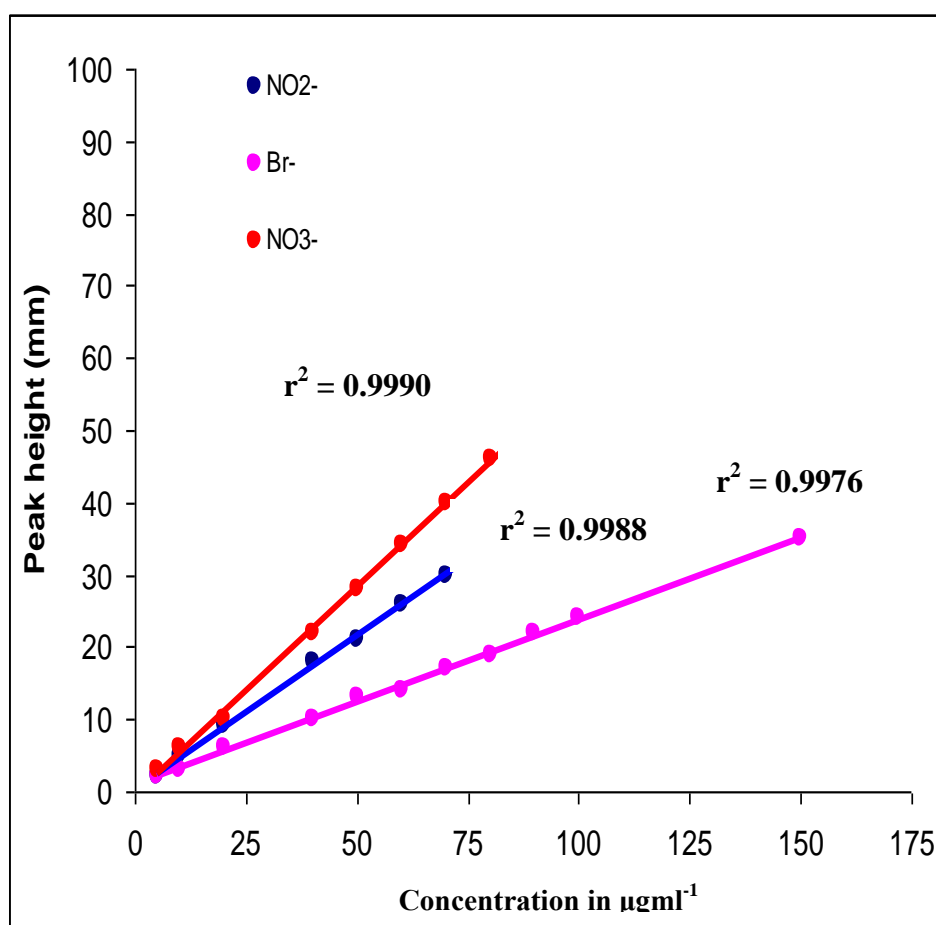


Fig. 6 Calibration graph for anions

Table 2 Calibration data of the three ions separated and determinate by the home – made ion chromatography

Ions	Linear range $\mu\text{g ml}^{-1}$	Correlation coefficients	Detection limits $\mu\text{g ml}^{-1}$
NO_2^-	5 - 70	0.9988	0.050
Br^-	5 - 150	0.9976	0.500
NO_3^-	5 - 80	0.9990	0.075

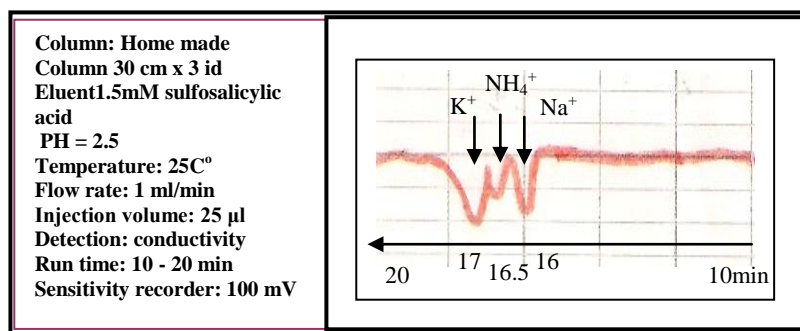


Fig. 7 Separation of $50 \mu\text{g mL}^{-1}$ Na^+ , NH_4^+ , and K^+ ions

Effects of 18-crown-6-ether concentration

The relationship between the addition of 18-crown-6-ether concentration and retention time behavior against sulfosalicylic acid eluent was improved (fig.8). The Rt of anions NO_2^- , Br^- and NO_3^- particularly increased. Retention time of cations Na^+ , NH_4^+ and K^+ were similarly increased according to 18 - crown - 6 - ether addition concentration, as show in Figure 8.

The increased of concentration of 18- crown -6- ether particularly shift the bands of cations. Rt values of the anions slightly effect where for mono cations especially potassium (K^+) ion which showed an increase. Higher Rt, this behavior can be explain by

the stability constants for complexes of the alkali metal ions with 18 - crown - 6 - ether.

In order to improve the resolution of cations by using ion exchange, the relationship of 18-crown-6 ether addition concentration and retention behavior against Sulfosalicylic acid eluents. Even through the retention time of anions were not particularly changed, Retention time of potassium ion K^+ was similarly increased according to 18-crown-6-ether addition concentration (Kwon *et al.* and Connolly). As shown in fig. 8.

Complexation stability constants of crown ether inside radius of crown ether and cation radius have largely influenced on the formation of complex (Schaller, Davey).

Figure 9 shows the effect of 18-crown-6- ether concentration added to 1.5 mM Sulfosalicylic acid eluent on peak height. These results indicated that peak height for anions

not effected and stay established in this study. Fig.10 shows the separation of mono anions and cations in sulfosalicylic acid and 18-crown-6-ether.

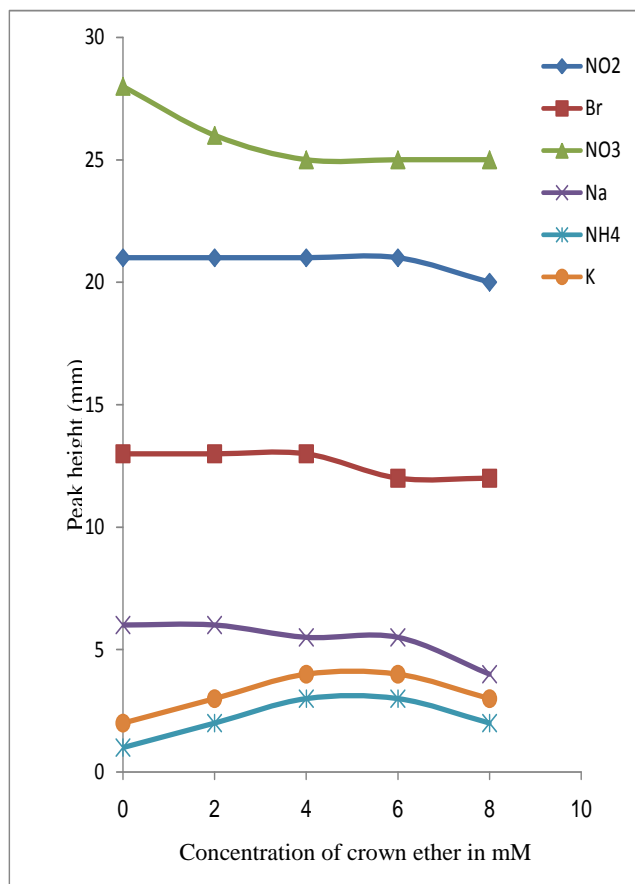


Fig.9 Effect of 18-crown-6-ether Concentration on Retention time of anions and captions

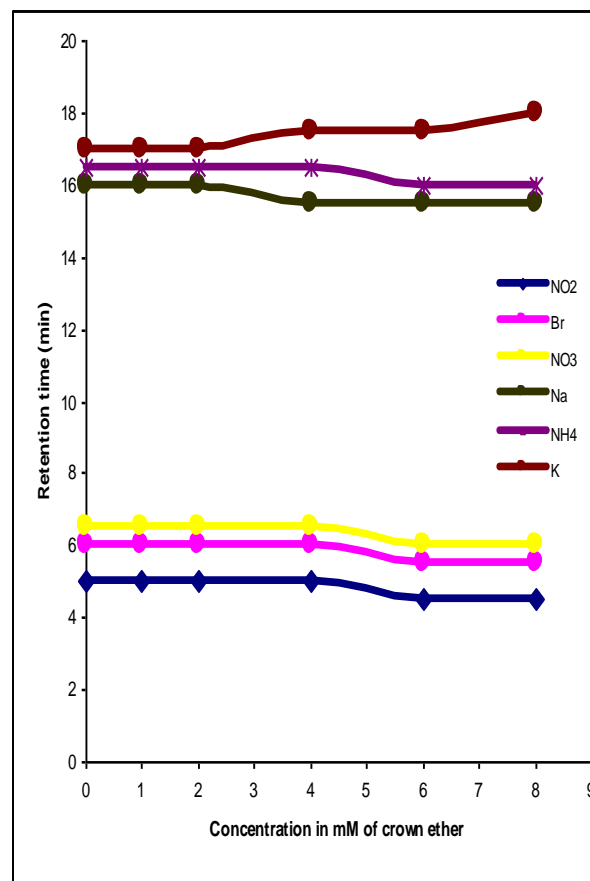


Fig.8 Effect of 18-crown-6-ether Concentration on Retention time of anions and cations

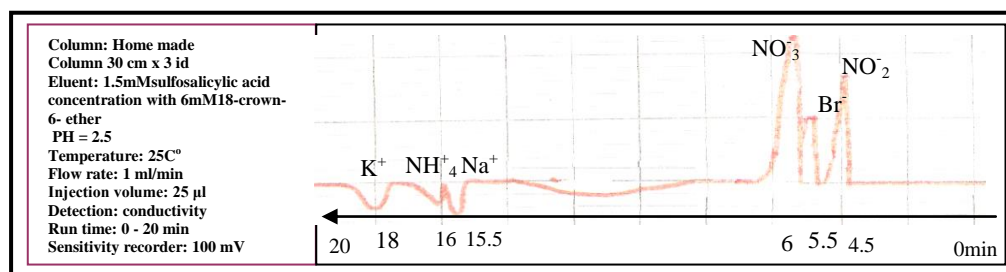


Fig.10 Separation of mono anions and cations in sulfosalicylic acid and 18- crown -6-ether eluents

Calibration graph for separation cations

Under the optimum conditions described in table (1) using the proposed home – made IC system in fig.1, calibration

graph was obtained for sodium , ammonium ,and potassium by plotting the graph of peak height (mm) Vs concentration ($\mu\text{g mL}^{-1}$) as show in figure 11. Three chromatograms were used for each concentration. The peak height increase with increasing the concentration , a linear range of

$1 - 140 \mu\text{g mL}^{-1}$, $5 - 100 \mu\text{g mL}^{-1}$, and $1 - 120 \mu\text{g mL}^{-1}$ for sodium , ammonium ,and potassium ions respectively

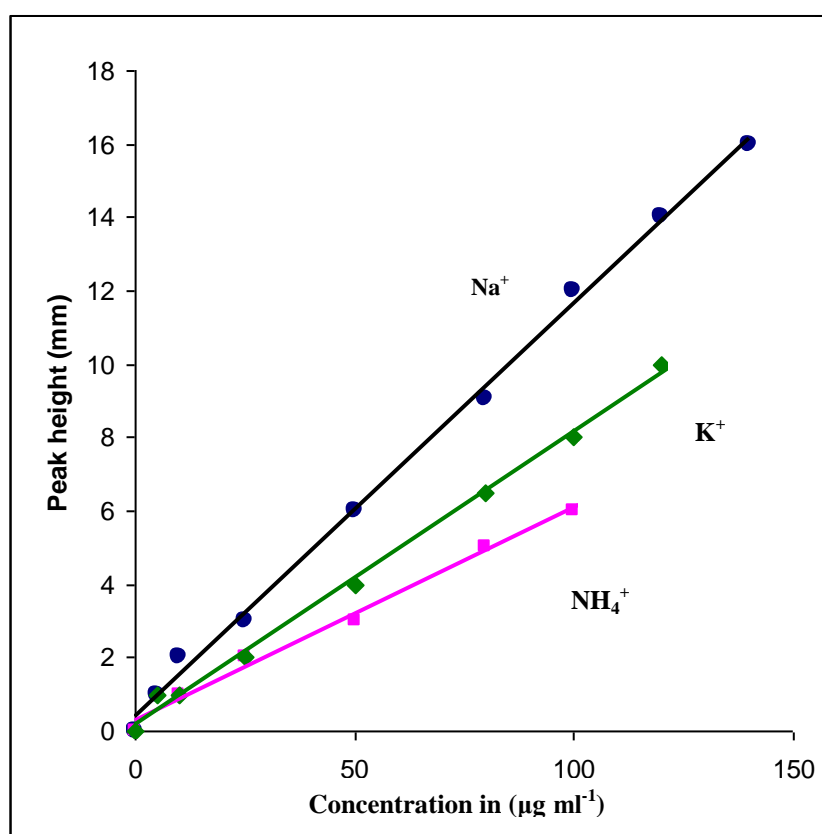


Fig. 11 Calibration graph for three cations Na^+ , NH_4^+ , and K^+

Analytical performance characterize

By using the home made ion chromatography system which operated at the optimum conditions which established in this study. A linear calibration plot of the average of triplicates peak height versus concentration for three cations was obtained as show in table 3.

The reproducibility of retention time and peak height under optimum conditions are reported for anions. Relative standard deviations (r. s. d %) was calculated for three chromatographic runs for each anion. The values obtained were between 0.45 – 0.90 % and 0.42 – 0.91 % for peak height and retention times for the three anions (nitrate, nitrite, and bromide).

Relative standard deviation r.s.d % were calculated also for three chromatographic runs for each cations (sodium , ammonium ,and potassium) .The values obtained were between 0.166 – 0. 250 % and 0. 29 – 0. 48 % for peak height and retention times, respectively.

Table 4 shows relative standard deviation of peak height and retention times for anions eluted with 1.5 mM Sulfosalicylic acid and 18 - crown -6-ether three and table 5 show relative standard

deviation of peak height and retention time for cations eluted with 1.5 mM Sulfosalicylic acid and - crown -6- ether(Lu bi and Kampus, Hussein).

Table 3 Calibration data of the three ions separated and determinate by the home – made ion chromatography

ions	Linear range $\mu\text{g ml}^{-1}$	Correlation confections	Detection limits $\mu\text{g ml}^{-1}$
Na^+	1 – 140	0.9969	0.15
NH_4^+	5 – 100	0.9897	0.25
K^+	1 – 120	0.9958	0.25

Table 4 Relative standard deviation of peak height and retention times for anions Eluted with 1.5 mM Sulfosalicylic acid and 6mM 18- crown -6- ether

Anions $50 \mu\text{g ml}^{-1}$ of mixture	Peak height r.s.d%	Retention time r.s.d%
NO_2^-	0.45	0.91
Br^-	0.90	0.47
NO_3^-	0.51	0.42

Table 5 Relative standard deviation of peak height and retention times for cations eluted with 1.5 mM Sulfosalicylic acid and 6mM 18- crown -6- ether

Cations ($50 \mu\text{g ml}^{-1}$ of mixture)	Peak height r. s. d%	Retention time r. s. d%
Na^+	0.166	0.32
NH_4^+	0.250	0.29
K^+	0.217	0.48

Application

The home-made semi-automated IC system was used successfully to the separation and determination of many water samples. The chromatograms presented in Figures 12, 13 and 14 show that separation of some anions and cations and some pharmaceutical preparations.

The peaks resolution was quite satisfactory and easily to identify the separated ions from their retention times .The figures also show that anions eluted earlier that than cations from column .This thought to be due to

ion exclusion and typical ion exchange mechanisms for separation the anions and cations respectively (Bhattacharyya and Rohrer)

Conclusions

This home-made ion chromatography system can be applying for simultaneous analysis of anions and cations in routine analysis for common inorganic anions and cations in different water samples (tap, drinking, and rain water) and some pharmaceutical preparations.

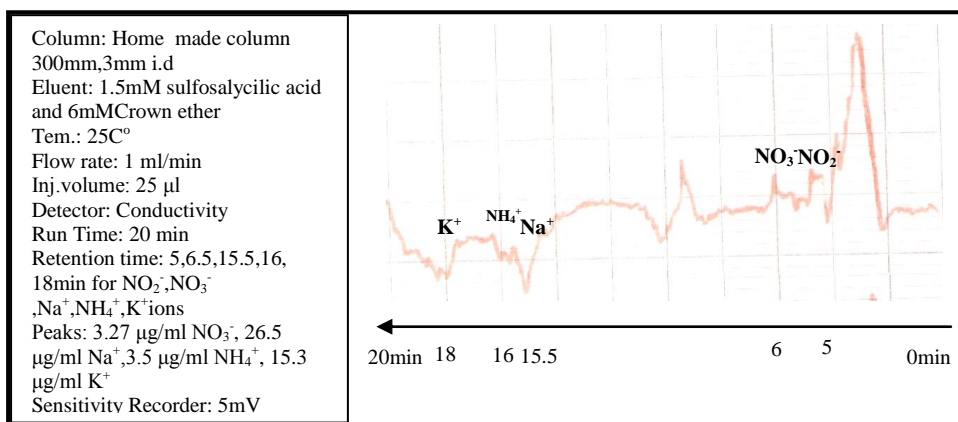


Fig. 12 Separation of some ions in tap water sample

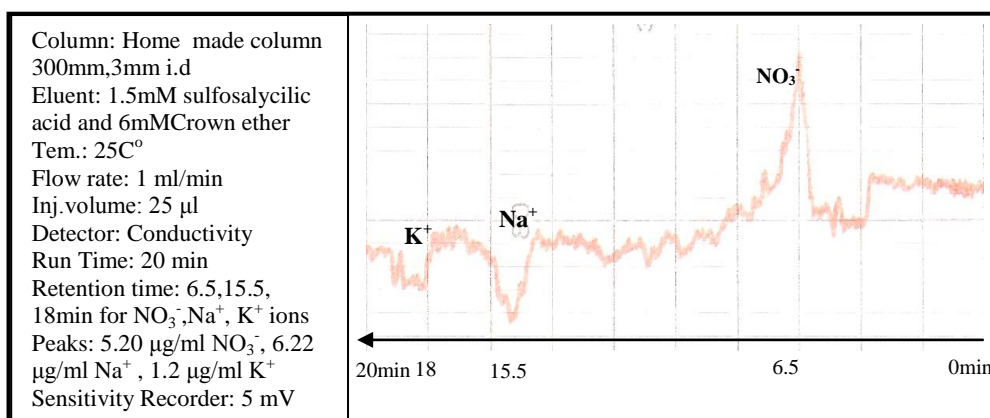


Fig. 13 Separation of some ions in drinking water sample

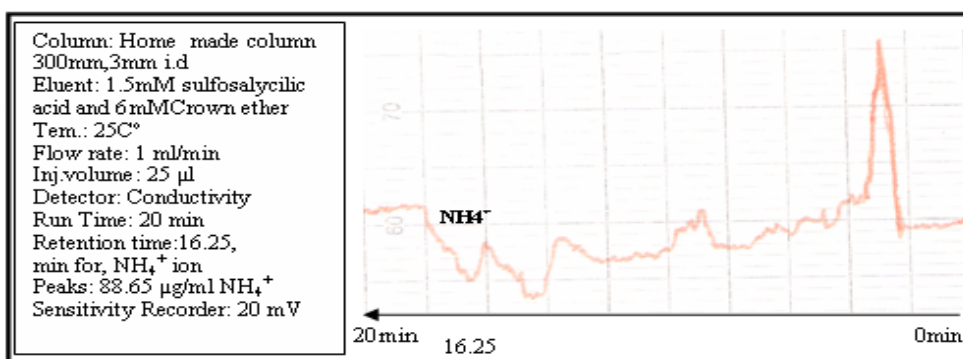


Fig.14 Separation ammonium ion in pharmaceutical preparation Isilin

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التقدير الآتي لبعض الايونات الموجبة و السالبة بنظام كروماتوغرافي أيوني**كامل حسين السوداني و خوله سلمان عبد الرسول****قسم الكيمياء - كلية التربية للعلوم الصرفة - جامعة البصرة - العراق****dr.alsowdanifia@yahoo.com****الخلاصة:-**

وصفت طريقة لتحليل الأني للأيونات السالبة و الموجبة بنظام الأيون كروماتوغرافي مصمم محليا باستخدام مقياس التوصيلية، استعمل مزيج من حامض السلفو سلسلك مع الكروان أيثر كمزيج مناسب للأيونات السالبة والموجبة وباستخدام مقياس التوصيلية . حضر عمود الفصل الكروماتوغرافي باستخدام مزيج من المبادل الحامضي الضعيف والمبادل القاعدي الضعيف وينسب متساوية .

تحت الظروف الفضلى للدراسة كانت الخطية بحدود (5 -150 µg/ml) و (1 - 140 µg/ml) للأيونات السالبة و الموجبة على التوالي بمعامل ارتباط (0.9978 - 0.9995) و (0.9899 - 0.9965) للأيونات السالبة و الموجبة على التوالي و وجد إن حدود الكشف هي (0.075 - 0.500) و (0.15 - 0.25) للأيونات السالبة و الموجبة على التوالي ومنحني الانحراف القياسي النسبي % \pm r.s.d بحدود (0.166 % - 0.250) و (0.45 - 90 %) لارتفاع القمة للأيونات السالبة و الموجبة على التوالي ،. طبقت هذه الطريقة بنجاح لتقدير الأيونات الموجبة والسالبة في الماء وبعض المستحضرات الصيدلانية.