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Ion chromatographic method for the determination of cations of group IA and IIA in water samples, pharmaceuticals and energy drinks by non-suppressed conductometric detection

Research Article

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Abstract: An efficient ion chromatographic (IC) method was developed for the simultaneous quantitative determination of Li^+, Na^+, NH_4^+, K^+, Cs^+, Ca^{2+} Mg^{2+}, Sr^{2+}, Ba^{2+} and Be^{2+} in energy drinks, pharmaceutical and drinking water samples by non-suppressed conductometric detection. The separation of ten cations including ammonium was achieved using a cation-exchange column and low conductivity mobile phase. The mobile phase consisted of tartaric acid, dipicolinic acid and boric acid. The separation of the cations was completed in less than 18 min, with a flow rate of 1.2 mL min^{-1}. The separation was not affected by the existence of cations Co^{2+}, Cr^{3+}, Cd^{2+}, Cu^{2+}, Bi^{3+}, Ag^+, Fe^{3+} and Zn^{2+} in concentrations up to 20 mg L^{-1}. Using an injection volume of 20 μL the obtained detection limits were 0.003 mg L^{-1}, 0.02 mg L^{-1}, 0.01 mg L^{-1}, 0.01 mg L^{-1}, 0.10 mg L^{-1}, 0.01 mg L^{-1}, 0.02 mg L^{-1}, 0.02 mg L^{-1}, 0.003 mg L^{-1} and 0.1 mg L^{-1}, for Li^+, Na^+, NH_4^+, K^+, Cs^+, Ca^{2+} Mg^{2+}, Sr^{2+}, Be^{2+} and Ba^{2+} respectively. The intra-day repeatability (RSD%, n=5) ranged from 1.1% to 4.8%, and the inter-day (n=5) between 1.8% and 5.4% respectively. The method was applied to the analysis of various bottled and tap water, pharmaceutical preparations and energy drinks commercially available.

Keywords: *Ion chromatography • Cations • Water • Pharmaceutical preparations • Energy drinks.*

1. Introduction

Ion chromatography has become a widely used analytical technique for the determination and separation of cationic analytes in various sample matrices and at very low level. Common cations such as Li^+, Na^+, K^+, Ca^{2+} and Mg^{2+} are present in water and isotonic drinks samples and play a vital role in the function of biological systems in the human body.

Conductometric detectors were employed in several reported methods, either by using suppressed or non-suppressed conductivity acquisition [1-9]. Six common cations have been determined by Kim and Lee [4], by using a Waters IC-PAK CM/D column and a mixture of HNO_3 and EDTA as eluent. In addition, Thomas *et al*. [7] applied an ion chromatography method with a high-capacity cation-exchange IonPac CS16 column which separated alkali, alkaline earth and ammonium cations in environmental waters. Recently, a study has been carried out in reference to the chromatographic behaviour of monovalent and divalent cations, based on propylsulfonic acid functionalized silica stationary phase [9]. Low cost paired emitter–detector diode (PEDD) [5] and indirect photometric detection (IPD) [6] are two additional types of detectors reported in the literature for the simultaneous designation of cations besides the conductivity detectors.

In several cases, other elements are also determined together with common heavy metal cations such as cobalt, nickel, iron, cadmium and zinc, *etc*. [10,11].

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A single-column IC method was performed for the determination of copper, lithium, sodium, ammonium, potassium, cobalt, nickel, magnesium, calcium, strontium and zinc, with the use of an isocratic elution containing 2.5 mM methane-sulfonic acid using an IonPac SCS1 as separation column [12].

Ion chromatography could also be regarded as a powerful tool for separation and analysis of ions on non-alcoholic and alcoholic drinks i.e. isotonic beverages and wine [13]. A useful separation based on isocratic elution has been reported by Trifiro *et al*. [14], as far as the simultaneous separation and determination of Na^+, Ca^{2+}, Mg^{2+}, K^+ and NH_4^+ in fruit juices is concerned. Furthermore, Zenga *et al*. [12] developed a robust and sensitive method which allowed the simultaneous separation of eleven cations in one chromatography run in beer, without interferences. Ding *et al*. [15] determined various cations in wine, Japanese sake and instant coffee powder, without following any special sample pre-treatment procedure. Moreover, simultaneous determination of organic acids and cations [16], and anions and cations [17] in beverages were reported by using a quite simple mobile phase with a column switching technique.

Another application where IC may be employed is the analysis of pharmaceutical preparations. Cations like Na^+, K^+ and Ca^{2+} which are included in these formulations are of crucial importance for the electrolyte balance in human body. Bashir and Paull [18] described a selective method, in which medicinal NaCl saline solution was analysed by using post-column reaction with o-cresolphthalein complexone. Moreover, two additional papers have focused on the simultaneous determination of cations in drug substances by applying this technique [19,20]. Nevertheless the potential of ion chromatography for the analysis of cations in various other matrices needs to be further investigated since it is a convenient and relatively low cost technique.

Therefore, the purpose of the present study was to develop and validate an IC method, aiming to the separation and determination of five monovalent and five divalent cations from groups IA and IIA, including ammonium; by using a cation exchange column and a low conductivity mobile phase consisting of three weak acids, *i.e*., tartaric, dipicolinic and boric acid. After its optimization, the developed method was applied in water samples, pharmaceutical preparations and energy drinks, which have been very widely consumed in recent years. It should be noted that as far as we know, no other similar methods are reported in literature for the analysis of such drinks.

2. Experimental procedure

2.1 Instrumentation

The ion chromatographic system consisted of a Shimadzu (Kyoto, Japan) isocratic parallel-type double plunger pump (LC-20AD), a Rheodyne model 9725(i) injection valve, (Rheodyne, Cotati California, U.S.A), equipped with a 20 μL sample volume, a controller (Shimadzu CBM-20A) and a conductivity detector (Shimadzu CDD-10AVP), allowing to monitor various ions by non-suppressed system. A guard column IC (YK-G) and an IC (YK-421) (125×4.6 mm I.D.) cation-exchange column with carboxylic functional group, were employed for cations separation. Both columns were obtained from Shodex [21]. Although the column nominal theoretical plates N are ca. 2800, the current values in the employed column ranged between 1200 and 1700 for various ions due to previous long use. Detection cell and columns were placed in a Shimadzu (CTO-20AC) column oven. LC Solution (Version 1.25) was the software used. A Transonic 460/H Ultrasonic bath (Elma, Germany) was chosen for degassing the solvents prior to use. A sample volume of 20 μL was injected in all cases.

A Perkin Elmer 3100 XL Axial Viewing Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) was employed for comparative determination of Cs^+, Sr^{2+}, Ba^{2+} and Be^{2+}. Flame atomic absorption analysis was also employed for Ca^{2+} and Mg^{2+} data using a Perkin Elmer 5100 AAS instrument. In addition, UV-Vis spectrometry (indophenol blue method) for NH_4^+ determination and Flame Atomic Emission Spectrometry (FAES), for Li^+, Na^+ and K^+ were applied. The above methods were used as standard reference methods [21] for comparative purposes.

2.2 Reagents and solutions

Standard solutions with a certified concentration 1000 mg L^{-1} for each of the ions of Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Be^{2+}, Co^{2+}, Cr^{3+}, Cd^{2+}, Cu^{2+}, Bi^{3+}, Ag^+, Fe^{3+} and Zn^{2+} were supplied by Merck (Darmstadt, Germany). In particular, standard solutions of NH_4^+, Cs^+ and Sr^{2+}, (1000 mg L^{-1}) were prepared from pro-analysis grade salts of NH_4Cl, CsCl and $SrCl_2 \cdot 6H_2O$ respectively, which were purchased from Merck (Darmstadt, Germany). Working standards, of ions for calibration, were prepared by further dilution of the 1000 mg L^{-1} standard solutions.

The examined mobile phases were prepared by dissolving analytical-reagent grade tartaric acid, dipicolinic acid and boric acid (Merck, Darmstadt,

Germany) in Milli-Q grade water. Ultra-pure water was prepared by passing deionized water through a Milli-Q (18.2 MΩ cm^{-1}) purification system (Bedford, MA, USA), and was used to prepare standard solutions of cations and mobile phases. The standard solutions were stored at ambient temperature, showing not changes in concentration of the analytes for at least one month. A simple dilution with Milli-Q grade water, 1:1, 1:100 1:200 or 1:1000 (v/v), was sufficient in order to ensure cations concentration falling within the linear range of the calibration function.

Both diluted samples and mobile phases were filtered through a 0.45 μm membrane filter and degassed before injection into the chromatographic system.

3. Results and discussion

3.1 Optimization of IC separation

Tartaric and dipicolinic acid have been used in ion chromatography with non-suppressed conductivity measurement [22,23] while boric acid has also been useful for pH adjustment [21] and recommended by the column manufacturer. The triple mixture mobile phase's pH was 2.92±0.07, while the examined dual mixtures of tartaric acid - dipicolinic acid and tartaric acid - boric acid were 3.22±0.05 and 3.41±0.09 respectively. The optimum mobile phase composition were 5 mM tartaric acid, 1 mM dipicolinic acid and 24 mM boric acid, providing better resolution among the different peaks and fast separation of analytes. The selected optimum mobile phase does not permit satisfactory separation of Na^+ and NH_4^+ peaks in presence of high sodium concentration and allows only quantitative determination of sodium and ammonium in much lower Na^+:NH_4^+ concentration ratios. This is also reflected to the resolution factor between Na^+:NH_4^+ peaks. In particular, when solutions of high concentrations of Na^+ were analyzed, the calculated resolution factor was 0.6 for Na^+ - NH_4^+. Nevertheless, under low concentrations of Na^+, the obtained resolution factor was almost 1.6 for Na^+ - NH_4^+ as depicted in Fig. 1. In Table 1 obtained resolution factor for Na^+ - NH_4^+ pairs in several concentration ratios are presented. Thus, the quantitative determination of NH_4^+ is allowed as long as the resolution factor of Na^+ and NH_4^+ peaks is adequate.

In order to optimize the separation and detection of these ten cations, different flow rates, from 0.8 to 1.3 mL min^{-1}, were also investigated by isocratic elution. The results showed that at higher flow rates peaks of Na^+, NH_4^+ and K^+ resolve better. The resolution factors of Na^+ - NH_4^+ and of NH_4^+ - K^+ pairs were increased by 0.2, while for the others no significant improvement was observed. Finally the optimum separation of ten cations was adjusted to 1.2 mL min^{-1} since this flow rate showed a better separation for the investigated ions.

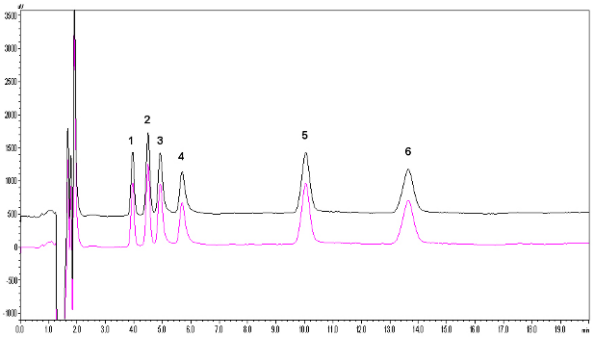

Figure 1. Ion chromatograms from the analysis of standard solution containing low concentration of sodium and high concentration of ammonium. 1) Na^+, 2) NH_4^+, 3) K^+, 4) Ca^{2+}, 5) Mg^{2+}.

Table 1. Resolution factor for the Na^+ - NH_4^+ pair in several ratios

Na:NH_4^+ concentration ratios (in mg L^{-1})	Resolution factor for Na^+ - NH_4^+
0.8 : 1.0	1.6
3.0 : 0.1	0.6
5.0 : 1.0	0.5
10.0 : 0.1	0.4

The effect of temperature was simultaneously studied for ten cations, at temperatures of 30, 35, 40, 45 and 50°C respectively. However, both the conductimetric cell and the separation column were heated simultaneously, limiting the ability to study the effect of temperature on column separation. Eventually the optimum separation of cations was observed at 40°C. Typical repeatable chromatograms illustrating the separation of the cations at this temperature are given in Fig. 2, which were obtained by injecting a mixture of standards of the ten analytes.

3.2 Method validation

Performance characteristics, such as linearity, detection limits (LOD), quantitation limits (LOQ) and repeatability for each of the ten analytes were evaluated using multi-analyte standards, which contained all ten cations under optimum conditions. It was observed, that all analytes could be detected with excellent linearity within the concentration range examined. Satisfactory correlation coefficients between analyte concentration and peak area signals were obtained ($r > 0.962$) for all analytes. In addition, the detection and quantitation limits were determined from the signal to noise ration of standard

solutions. Detection limit values generally varied from 0.003 to 0.10 mg L^{-1} depending on the analyte. The ammonium performance was studied in absence of sodium concentration. The analytical performance characteristics of the proposed method for each cation are summarized in Table 2.

The repeatability was assessed by the relative standard deviation (RSD, %) of five replicate injections, ranged from 1.1 % to 4.8%, and 1.8% to 5.4% for intra-day and inter-day analysis, respectively.

To estimate the accuracy of the method, three samples, *i.e.*, water, energy drink and isotonic solution were spiked with known concentrations for all ten ions in order to calculate the recoveries of the developed IC method (Table 3). The concentrations of not spiked samples in Table 3 refer to finally diluted samples. The obtained analyte recoveries (95.1–104.0%) showed that no significant carryover effects, due to the presence of other ingredients in the analysed samples, were observed during the sample analysis. No interferences from the presence of several other metal ions like cobalt, *i.e.*, Co^{2+}, Cr^{3+}, Cd^{2+}, Cu^{2+}, Bi^{3+}, Ag^{+}, Fe^{3+} and Zn^{2+}, were observed when these ions are present at concentrations up to 20 mg L^{-1}. The studied cations do not create potential interferences since the used stationary – mobile phase system is not favorable for retention of these cations.

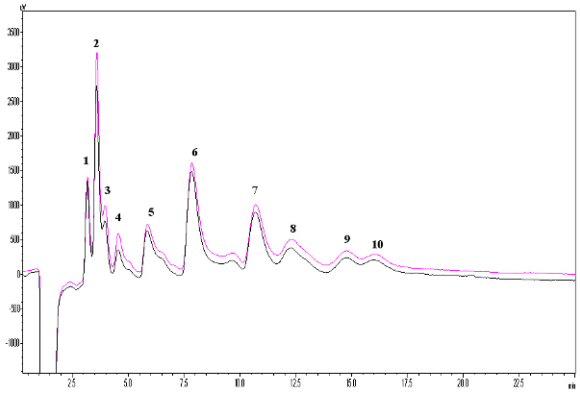

Figure 2. Typical repeatable chromatograms for the simultaneous determination of ten cations. Concentrations of cations: 1) Li^{+} = 0.2 mg L^{-1}, 2) Na^{+}= 2.0 mg L^{-1}, 3) NH_4^{+}= 0.1 mg L^{-1}, 4) K^{+}= 1.0 mg L^{-1}, 5) Cs^{+}= 10.0 mg L^{-1}, 6) Ca^{2+}= 4.0 mg L^{-1}, 7) Mg^{2+}= 1.5 mg L^{-1}, 8) Sr^{2+}= 2.0 mg L^{-1}, 9) Be^{2+}= 0.2 mg L^{-1}, 10) Ba^{2+}= 3.0 mg L^{-1}.

In comparison to previously published methods for other matrices, the proposed one offers some important advantages. In particular, ten cations could be separated and determined, instead of seven [1] or six cations [4,7]. Beryllium was also included in the analytes and eventually it was possible to be determined. Furthermore, the detection limits were lower for Na^{+}, NH_4^{+}, K^{+}, Mg^{2+}, Ca^{2+}, and higher for Li^{+}, Na^{+}, K^{+}, Mg^{2+}, in comparison with those obtained by Amin *et al*. [3] and Zeng *et al*. [12], respectively. The feasibility of the method in various matrices, as described below, is also another of its features.

3.3 Applications

The method could be applied either to natural waters, pharmaceutical preparations, nutritional products and energy drinks, which are widely consumed. It has to be mentioned that no other similar methods are reported in literature, for such drinks, as far as we know. Example

Table 2. Analytical performance characteristics of the proposed method

Analyte	Sensitivity (Slope)	Correlation coefficient (r)	LOD (mg L^{-1})	LOQ (mg L^{-1})
Li^{+}	53×10^3	0.999	0.003	0.010
Na^{+}	9×10^3	0.987	0.020	0.060
NH_4^{+*}	9×10^3	0.983	0.010	0.030
K^{+}	6×10^3	0.997	0.010	0.030
Cs^{+}	1×10^3	0.986	0.100	0.400
Ca^{2+}	5×10^3	0.991	0.010	0.030
Mg^{2+}	12×10^3	0.998	0.020	0.070
Sr^{2+}	5×10^3	0.989	0.020	0.060
Be^{2+}	39×10^3	0.986	0.003	0.009
Ba^{2+}	2×10^3	0.993	0.100	0.300

**Ammonium performance was studied in absence of sodium concentration.*

Table 3. Recoveries of cations in three spiked real samples.

Analyte	Sample	Not spiked (mg L^{-1})	Spiked		Recovery (%)
			Added (mg L^{-1})	Found (mg L^{-1})	
Li^+	Water[a]	-	0.100	0.096	96.0
	Energy drink[b]	-	0.100	0.097	97.0
	Isotonic solution[c]	-	0.100	0.102	102.0
Na^+	Water[a]	3.245	1.000	4.258	101.3
	Energy drink[b]	3.750	1.000	4.701	95.1
	Isotonic solution[c]	3.738	1.000	4.699	96.1
K^+	Water[a]	0.725	0.500	1.222	99.4
	Energy drink[b]	0.892	0.500	1.402	102.0
	Isotonic solution[c]	0.263	0.500	0.759	99.2
Cs^+	Water[a]	-	5.000	5.030	100.6
	Energy drink[b]	-	5.000	4.980	99.6
	Isotonic solution[c]	-	5.000	4.890	97.8
Ca^{2+}	Water[a]	31.000	2.000	32.990	99.5
	Energy drink[b]	1.270	2.000	3.320	102.5
	Isotonic solution[c]	-	2.000	1.980	99.0
Mg^{2+}	Water[a]	11.100	0.750	11.840	98.6
	Energy drink[b]	1.440	0.750	2.200	101.3
	Isotonic solution[c]	-	0.750	0.770	102.6
Sr^{2+}	Water[a]	-	1.000	1.040	104.0
	Energy drink[b]	-	1.000	1.030	103.0
	Isotonic solution[c]	-	1.000	0.980	98.0
Be^{2+}	Water[a]	-	0.100	0.097	97.0
	Energy drink[b]	-	0.100	0.099	99.0
	Isotonic solution[c]	-	0.100	0.096	96.0
Ba^{2+}	Water[a]	-	1.500	1.500	100.0
	Energy drink[b]	-	1.500	1.490	99.3
	Isotonic solution[c]	-	1.500	1.510	100.6

[a] Measurement with 2-fold dilution. [b] Measurement with 100-fold dilution. [c] Measurement with 1000-fold dilution.

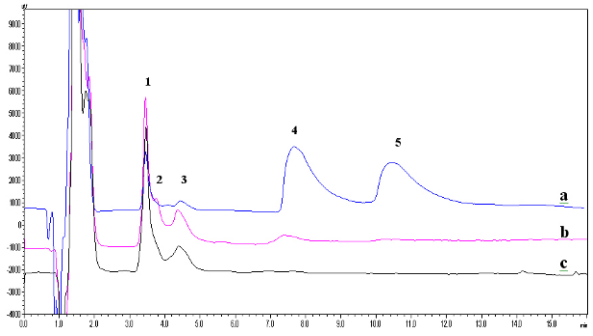

Figure 3. Ion chromatograms from the analysis of: (a) a drinking water sample; (b) intravascular isotonic solution; (c) energy drink. 1) Na^+, 2) NH_4^+, 3) K^+, 4) Ca^{2+}, 5) Mg^{2+}.

of chromatograms obtained from the analysis of drinking water and also for an intravascular isotonic solution and an energy drink are illustrated in Fig. 3.

3.3.1. Bottled and tap water

Six commercial brands of still and carbonated bottled waters (assigned as BK, IL, ZG, KR, MT and BG) and two samples of tap waters (assigned as TP1, TP2) were analysed. The total contents of the ten cations in water samples were measured directly by using the developed IC method. The results are in satisfactory agreement with those indicated on the labels of the bottled waters. In case of tap waters, good agreement was observed, in comparison with the results of standard methods which were applied in parallel, as it can be seen in Table 4. The obtained results demonstrated that the ammonium concentration was higher than the detection limit in the case of IL and KR samples.

3.3.2. Pharmaceutical and nutritional preparations

The purposed method was applied to lens cleaning solutions, infant nutritional products (RZ) and medicinal NaCl saline solutions, assigned as NO, RZ and NC respectively. The results are given in Table 4. In accordance with the results, the proposed IC method was proved to be efficient for the quantitative determination of mono- and divalent cations in pharmaceutical preparations. Apparently the calcium levels detected in RZ sample are due to the contained rice flour of this product.

Table 4. Determined results for inorganic cations in various samples (mean values from n = 5 replicates) using the proposed IC method and other reference standard methods.

Product	Conc. (mg L^{-1})	Li^+	Na^+	NH_4^+	K^+	Cs^+	Ca^{2+}	Mg^{2+}	Sr^{2+}	Be^{2+}	Ba^{2+}
TP1	Found[a]	-[f]	17.04	-	3.99	-	44.98	23.08	-	-	-
	Standard Method[e]	-	17.10	<0.02	4.10	-	46.00	23.00	-	-	-
TP2	Found[a]	-	12.63	-	3.36	-	47.07	17.28	-	-	-
	Standard Method[e]	-	12.10	<0.02	3.50	-	44.50	17.80	-	-	-
BK	Found[a]	-	2.93	-	0.42	-	90.40	3.14	-	-	-
	Labelled	-	2.80	<0.26	0.40	-	97.00	3.40	-	-	-
IL	Found[a]	-	6.49	D[g]	1.45	-	62.01	22.21	-	-	-
	Labelled	-	6.56	<0.2	<2.00	-	66.33	21.29	-	-	-
ZG	Found[a]	-	3.07	-	0.94	-	74.99	3.37	-	-	-
	Labelled	-	2.90	0	1.00	-	79.10	3.10	-	-	-
KR	Found[a]	-	4.14	D	0.84	-	94.50	2.25	-	-	-
	Labelled	-	4.10	<0.05	0.82	-	99.20	2.20	-	-	-
MT	Found[a]	-	2.72	-	0.59	-	89.17	1.90	-	-	-
	Labelled	-	2.60	<0.22	0.60	-	83.80	<2.70	-	-	-
BG	Found[a]	-	1.92	-	0.56	-	64.00	0.94	-	-	-
	Labelled	-	2.00	<0.26	0.60	-	64.10	1.00	-	-	-
RB	Found[b]	-	375	-	89.20	-	126.80	144.00	-	-	-
	Labelled	-	400	-	-	-	-	-	-	-	-
TF	Found[b]	-	331.3	-	41.80	-	-	-	-	-	-
	Labelled	-	<400	-	-	-	-	-	-	-	-
SH	Found[d]	-	596	-	70.90	-	-	-	-	-	-
	Labelled	-	-	-	-	-	-	-	-	-	-
NO	Found[d]	-	1478	7.6	-	-	1348	-	-	-	-
	Labelled	-	-	-	-	-	-	-	-	-	-
RZ	Found[c]	-	1399	-	788	-	532	-	-	-	-
	Labelled	-	1380	-	782	-	-	-	-	-	-
NC	Found[d]	-	3738	-	263	-	-	-	-	-	-
	Labelled	-	3540	-	-	-	-	-	-	-	-

[a] *Measurement with 2-fold dilution.*
[b] *Measurement with 100-fold dilution.*
[c] *Measurement with 200-fold dilution.*
[d] *Measurement with 1000-fold dilution.*
[e] *A standard method was employed for comparison: ICP-AES for Cs^+, Sr^{2+}, Ba^{2+} and Be^{2+}; FAAS or volumetric for Ca^{2+} and Mg^{2+}; UV-Vis spectrophotometric (indophenol blue) for NH_4^+; and FAES for Li^+, Na^+ and K^+.*
[f] *Not detected*
[g] *Detected*

3.3.3. Energy drinks

Three types of energy drinks assigned as RB, TF and SH available in the market were analysed. The total concentrations of ten cations in the studied energy drinks were determined after 10-fold up to 100-fold dilution. The obtained results are listed in Table 4. The results are in good agreement with the levels of potassium labelled.

4. Conclusions

Monovalent (Li^+, Na^+, NH_4^+, K^+ and Cs^+) and divalent cations (Ca^{2+}, Mg^{2+}, Sr^{2+}, Be^{2+} and Ba^{2+}) could be determined by using a cation-exchange column with carboxylic functional group and a mobile phase consisting of weak acids like tartaric, dipicolinic and boric acid in relatively low concentrations. The combination of a low conductivity mobile phase with a low strength exchange column allows performing non-suppressed conductivity measurements with very good performance characteristics. Since minimum sample handling is required, the overall sample analysis time of the ten cations was less than 18 min. In addition, due to its satisfactory repeatability and reasonable linearity, the developed IC method was proved to be reliable for the determination of ten analytes in water samples, energy drinks and pharmaceutical formulations, showing good chromatographic profiles. The minimum sample preparation required and the low detection limits were the most important advantages of the proposed method.

Despite of the fact that analytes like Cs^+ or Be^{2+} were not detected in such samples, the possibility of contamination is still significant in any natural water sample or a contaminated one. Consequently, the ability to detect them is another feature of this method. Additionally, the method may be applicable to other natural and ground waters also, and to wastewaters as well.

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