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## A fast and convenient analysis method for the determination of cations in pomegranate juices by capillary electrophoresis with contactless conductivity detection

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**Abstract:** Health beneficial effect of pomegranate is mainly due to its confirmed high antioxidant capacity and polyphenolic content. In recent years, experimental and clinical studies have shown that pomegranate intake lowers blood pressure. Potassium and other minerals such as calcium and magnesium may be responsible for this property. In this study, a rapid, economic, reliable, and applicable capillary electrophoresis method was proposed with contactless conductivity detection for the quantitative determination of six cations in different pomegranate juices. The correlation between these cation contents of eight different pomegranate juices was evaluated by using one-way ANOVA and Duncan's multiple-range test. The optimum buffer composition was selected as 20 mM 3-(N-morpholino) propanesulfonic acid (MOPS) and 2.5 mM 18-crown-6 at pH 7.5. The proposed method was validated for  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Li}^+$  ions. These cations were quantified in different freshly squeezed and commercial pomegranate juices with recovery values between 94.1% and 103.1%. Potassium was found as the predominant mineral, reaching up to 2380 mg/L.

**Key words:** Capillary electrophoresis, contactless conductivity detector, pomegranate juice, potassium

### 1. Introduction

Pomegranate is a fruit that has attracted much attention in recent years due to its many beneficial effects on health. Antiinflammatory,<sup>1</sup> anticancer,<sup>2,3</sup> antiobesity,<sup>4</sup> and antihypertensive<sup>5,6</sup> effects are the subjects of many researches. Health beneficial effects of pomegranate are closely related with its antioxidant activity which is very high compared to many other fruits. Pomegranate contains a high amount of bioactive phenolics and other important nutrients like anthocyanins, amino acids, organic acids, and sugars.<sup>7–9</sup>

Hypertension is an important health problem that disturbs many people in the world. In addition to the development of new medicines in order to reduce hypertension, studies and perspectives are underway to keep hypertension under control by diet. While high sodium consumption increases blood pressure, observational studies and clinical trials indicate that the consumption of potassium in foods lowers high blood pressure.<sup>10</sup> In addition to potassium, Houston and Harper claimed that magnesium and calcium ions have shown positive effects on blood pressure control.<sup>10</sup> Fruits and their natural juices are good sources of these minerals and pomegranate juice consumption is extensive in Turkey.

The growing interest in pomegranate and pomegranate juice in recent years has also increased the interest in exploring the nutritional value of pomegranate juices from different parts of the world.<sup>9</sup> Besides the antioxidant activities, total phenolics, and bioactive contents of pomegranates from all over the world, the

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reports of minerals of pomegranate juices are very limited. The method used in these studies for the mineral quantification is usually the ICP-MS<sup>11,12</sup> or atomic absorption spectroscopy.<sup>13,14</sup> While antioxidant activities, total phenolics, and some other ingredients of pomegranate juices have been detected by simple spectroscopic or chromatographic methods, ICP-MS is more expensive than these methods and is not found in every laboratory. Atomic absorption analysis of juices needs time-consuming preparation steps like ignition of the samples and then dissolution in strong acids.

Capillary electrophoresis (CE) is a technique that has found a wide application field in food analysis with simple usage technique, separation speed, and separation efficiency.<sup>15</sup> After the capacitively coupled contactless conductivity detectors (C<sup>4</sup>D) have been combined with CE, CE-C<sup>4</sup>D has become a good alternative to IC for metal ions. C<sup>4</sup>D is suitable for detection of all poor or non-UV absorbing charged species and has many advantages over optical detection techniques. It provides low costs with highly sensitive detection for wide range of analytes including small ionic species. The detector cell surrounds capillary column and comprises two electrodes 2 mm apart from each other, one as actuator and the other is a pick-up.<sup>16</sup> These electrodes in the cell are not in galvanic contact with the solution where fouling or memory effect problems are inhibited with the aid of design. The electrical signal produced from the actuator electrode passes from the capillary and the signal arises collected by the pick-up electrode and the difference in the conductivities between background electrolyte and the analyte zones is detected. A detection window is not necessary; moreover, the design of the cell provides flexibility and compatibility with all type of capillary instruments and columns.<sup>16,17</sup> The recent applications of the CE-C<sup>4</sup>D method have been reviewed by Elbashir and coworkers.<sup>18,19</sup> De Carvalho et al. showed contactless conductivity detection of inorganic cations in mineral and phytotherapeutic formulations after CE separation.<sup>20</sup> To our knowledge, CE-C<sup>4</sup>D has not yet been applied to the analysis of nutritive minerals and NH<sub>4</sub><sup>+</sup> of fruit juices.

In this study, a rapid, economic, and reliable CE method coupled with C<sup>4</sup>D detection is proposed for the quantitative determination of main cations in both natural and commercial pomegranate juices in less than 4 min without the need for any time-consuming sample preparation procedure.

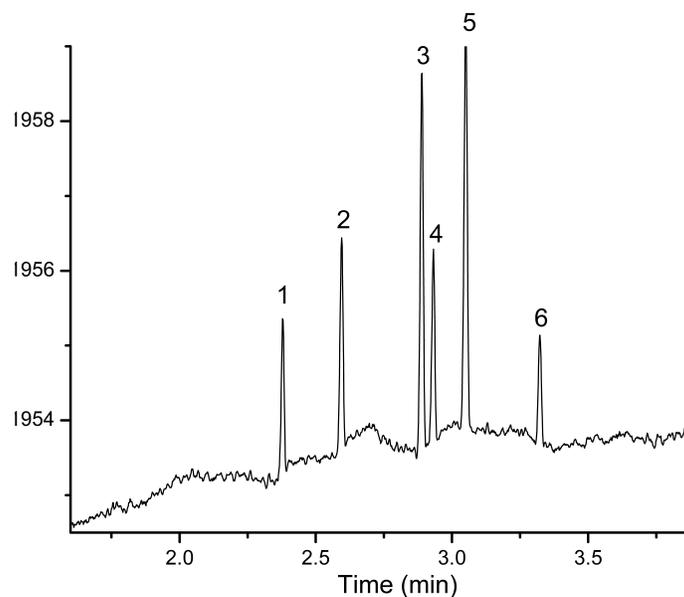
## 2. Results and discussion

### 2.1. Optimization of the separation conditions

Various separation media such as lactic acid, citric acid, ethylenediaminetetraacetic acid (EDTA), 4-(2-Hydroxyethyl)piperazine-1-ethanesulfonic acid (HEPES), and the 3-(N-morpholino) propanesulfonic acid (MOPS) were tested to obtain the best resolution conditions and peak symmetries for six cations.

For running buffer, the effect of pH on resolution of cations was studied in the range of 4 to 8. The pH values lower than 4 were not used due to rather high conductivity of running buffer and high signal to noise ratios. At high pH values, the high signal to noise ratios were also obtained. The small concentrations of acids were used due to their capacity of complexation with Ca<sup>2+</sup> and Mg<sup>2+</sup>. The good peak symmetries were not provided by these acids and some peak overlaps occurred, such as NH<sub>4</sub><sup>+</sup>/K<sup>+</sup> and Ca<sup>2+</sup>/Na<sup>+</sup>/Mg<sup>2+</sup>. At all tested buffer systems, the separation of NH<sub>4</sub><sup>+</sup> and K<sup>+</sup> was not achieved. Crown ethers have a suitable host cavity for K<sup>+</sup> ion as guest; therefore, 18-crown-6 was added to differentiate the mobility of the K<sup>+</sup> ions. The separation between NH<sub>4</sub><sup>+</sup> and K<sup>+</sup> was obtained by adding 18-crown-6 ether to all buffer systems. While both lactic and citric acids produced fluctuant baseline and also a high baseline signal, in the HEPES and EDTA solutions, very low resolution values were obtained. The poor resolutions between peaks and low peak heights were achieved with these types of tested acids.

MOPS was found as the most suitable running buffer for separation of six cations. Since pKa value of MOPS is 7.2, the pH of the buffer solutions prepared from MOPS was investigated between 6 and 8. At pH 6 a good resolution for cations was not obtained. The best resolutions, peak heights, and a uniform baseline were achieved at pH 7.5. The pH adjustments were made by Tris(hydroxymethyl)aminomethane (Tris) solution to inhibit the increase in conductivity of separation electrolyte. MOPS concentration was changed between 5 and 100 mM. Below 20 mM, the resolution between peaks was low. With the increasing concentrations of MOPS, the baseline noise increased and peak sensitivities decreased. According to the high peak signals and resolution between peaks, 20 mM MOPS was selected as the optimal concentration. The existence of 2.5 mM 18-crown-6 in 20 mM MOPS buffer was found sufficient for the resolution of  $\text{K}^+$  and  $\text{NH}_4^+$  peaks. The experiments were performed at the constant capillary column temperature of 20 °C in order to prevent increase in temperature. As a result of increase in temperature, the peaks, especially  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , were broadened. The separation voltage was decreased from 28 kV to 20 kV in order to obtain best resolutions between peaks of cations under optimum separation media by decreasing the rate of the EOF. Figure 1 represents the electropherogram of a mixture of standard solutions of six cations at optimum separation conditions. As seen from Figure 1, all ions migrate in a very short time of 3.5 min.



**Figure 1.** Electropherogram of 0.1 mM standard solution of cations except for  $\text{Li}^+$ . Its concentration is 0.2 mM. Optimized separation conditions, 20 mM MOPS, 2.5 mM 18-crown-6 at pH = 7.5, 20 kV, 60 mbar injection for 6 s from anodic side. Peaks: (1)  $\text{NH}_4^+$ , (2)  $\text{K}^+$ , (3)  $\text{Ca}^{2+}$ , (4)  $\text{Na}^+$ , (5)  $\text{Mg}^{2+}$ , (6)  $\text{Li}^+$ .

### 3. Method validation

Method linearity was tested by constructing five-point calibration curves against peak areas for each cation from 0.02 to 0.40 mM for  $\text{Ca}^{2+}$  and  $\text{Na}^+$ , from 0.02 to 0.80 mM for  $\text{K}^+$  and  $\text{Mg}^{2+}$ , and 0.03 to 0.80 mM and 0.05 to 0.80 mM for  $\text{Li}^+$  and  $\text{NH}_4^+$ , respectively. Calibration equations and good determination coefficients ( $R^2$ ) were listed with limit of detection (LOD) and limit of quantification (LOQ) values of six cations were given in Table 1. The LOD values were calculated as 3 times the signal to noise ratio and LOQs were found as 10 times the signal to noise ratio. Furthermore, the sample mass basis LODs were calculated for each cation using freshly squeezed pomegranate juice sample. The LOD values were found between 1.71  $\mu\text{g/L}$  and 210  $\mu\text{g/L}$ .

**Table 1.** Linearity equations for six cations, LOD, and LOQ values in  $\mu\text{M}$ .

Cation	Linear range mM	Regression equation	R <sup>2</sup>	LOD ( $\mu\text{M}$ )	LOQ ( $\mu\text{M}$ )
$\text{NH}_4^+$	0.05–0.80	$y = 1.915\text{E-}05x + 2.7263\text{E-}07$	0.9991	4.9	16.4
$\text{K}^+$	0.02–0.80	$y = 4.562\text{E-}05x - 1.090\text{E-}07$	0.9994	4.5	14.9
$\text{Ca}^{2+}$	0.02–0.40	$y = 7.050\text{E-}05x - 5.487\text{E-}07$	0.9996	2.3	7.7
$\text{Na}^+$	0.02–0.40	$y = 3.839\text{E-}05x + 5.374\text{E-}07$	0.9988	3.6	12.2
$\text{Mg}^{2+}$	0.02–0.80	$y = 8.762\text{E-}05x - 1.1834\text{E-}06$	0.9995	2.0	7.0
$\text{Li}^+$	0.03–0.80	$y = 2.364\text{E-}05x - 3.6142\text{E-}07$	0.9991	8.9	29.8

x: concentration of the ion (mM), y: corrected peak area.

The reproducibility results for migration times and corrected peak areas of cations were calculated for both intraday and interday injections and are given in Table 2. Five injections for the same day and five injections in each 3 consecutive days were performed. The recovery studies were applied to real sample of pomegranate juices by addition of standard solutions of cations in two different known concentration levels. Good recovery values (between 94.1% and 103.1%) were obtained and they are listed in Table 3.

**Table 2.** Reproducibility studies for the optimized method for six cations.

Cation	Intraday (n = 5)		Interday (n = 15)	
	Migration time (RSD%)	Corrected peak Area (RSD%)	Migration time (RSD%)	Corrected peak Area (RSD%)
$\text{NH}_4^+$	0.29	1.91	1.42	3.83
$\text{K}^+$	0.31	3.12	1.92	6.02
$\text{Ca}^{2+}$	0.25	4.42	0.83	5.98
$\text{Na}^+$	0.23	3.60	1.70	7.71
$\text{Mg}^{2+}$	0.28	3.79	2.08	5.57
$\text{Li}^+$	0.24	1.78	1.51	5.25

RSD %: Relative standard deviation.

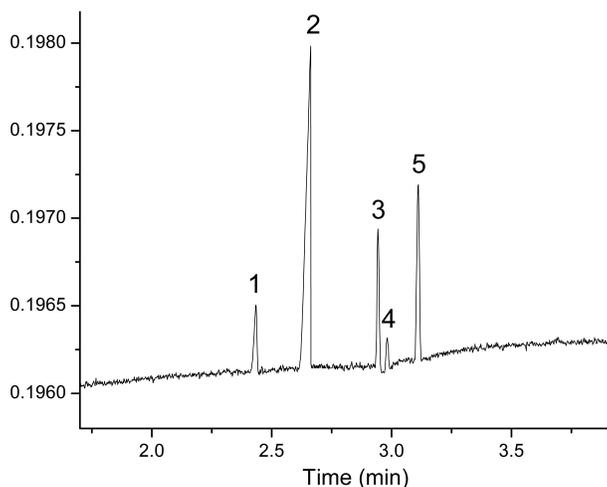
**Table 3.** Recovery values of six cations in real pomegranate juice sample.

Cation	Not spiked (mM)	Spiked (mM)	Found (mM)	Recovery %
$\text{NH}_4^+$	0.124	0.060 0.120	0.185 0.245	103.1 101.5
$\text{K}^+$	0.145	0.025 0.060	0.169 0.206	102.2 100.3
$\text{Ca}^{2+}$	0.086	0.050 0.100	0.134 0.182	95.3 96.0
$\text{Na}^+$	0.014	0.010 0.020	0.023 0.034	98.8 101.7
$\text{Mg}^{2+}$	0.101	0.050 0.100	0.152 0.204	102.8 103.1
$\text{Li}^+$	0	0.050 0.100	0.047 0.102	94.1 102.0

### 3.1. Method application to pomegranate juices

Eight different pomegranate juice samples were analyzed by the validated method. Inorganic cations were identified by spiking with standard samples. Figure 2 represents the electropherogram of a 25 times diluted

freshly squeezed pomegranate juice sample. Among the six common inorganic ions  $K^+$  amount is relatively higher in all pomegranate samples including freshly squeezed and commercially available samples.  $Li^+$  was not detected in juice samples.  $Na^+$  amounts were found significantly low compared to the other inorganic ions. The organic labeled pomegranate fruits juice ( $F_3$ ) has not shown any significant difference from other freshly squeezed juices except the  $NH_4^+$  values which was considerably lower than of the other pomegranates.



**Figure 2.** Twenty-five times diluted freshly squeezed organic ( $F_3$ ) pomegranate juice sample electropherogram. Separation conditions are the same as in Figure 1.

The amounts of cations found in the pomegranate juice samples are given in Table 4 as mg ion per L of juice sample and were calculated as average values of two injections.

**Table 4.** List of cations and their amounts in eight different pomegranate juices samples.

PJ samples	$NH_4^+$ (mg/L)	$K^+$ (mg/L)	$Ca^{2+}$ (mg/L)	$Na^+$ (mg/L)	$Mg^{2+}$ (mg /L)
<b>F<sub>1</sub></b>	205.80 ( $\pm$ 1.6) <sup>E</sup>	2252 ( $\pm$ 2) <sup>F</sup>	90.86 ( $\pm$ 1.78) <sup>D</sup>	11.72 ( $\pm$ 0.11) <sup>B</sup>	59.43 ( $\pm$ 0.24) <sup>B</sup>
<b>F<sub>2</sub></b>	162.10 ( $\pm$ 2.5) <sup>C</sup>	1631 ( $\pm$ 3) <sup>C</sup>	86.23 ( $\pm$ 0.63) <sup>C</sup>	7.451 ( $\pm$ 0.90) <sup>A</sup>	61.28 ( $\pm$ 0.30) <sup>B</sup>
<b>F<sub>3</sub></b>	16.52 ( $\pm$ 1.18) <sup>A</sup>	2124 ( $\pm$ 3) <sup>E</sup>	111.5 ( $\pm$ 2.9) <sup>E</sup>	7.776 ( $\pm$ 0.96) <sup>A</sup>	60.96 ( $\pm$ 2.44) <sup>B</sup>
<b>C<sub>1</sub></b>	187.30 ( $\pm$ 1.4) <sup>D</sup>	2036 ( $\pm$ 1) <sup>D</sup>	112.0 ( $\pm$ 1.2) <sup>E</sup>	41.27 ( $\pm$ 0.24) <sup>D</sup>	72.68 ( $\pm$ 0.68) <sup>C</sup>
<b>C<sub>2</sub></b>	222.30( $\pm$ 2.0) <sup>F</sup>	2380 ( $\pm$ 2) <sup>G</sup>	147.2 ( $\pm$ 2.9) <sup>F</sup>	29.87 ( $\pm$ 0.33) <sup>C</sup>	81.59 ( $\pm$ 0.59) <sup>D</sup>
<b>C<sub>3</sub></b>	223.20 ( $\pm$ 1.7) <sup>F</sup>	2274 ( $\pm$ 3) <sup>F</sup>	42.05 ( $\pm$ 0.19) <sup>B</sup>	153.0 ( $\pm$ 0.6) <sup>F</sup>	94.36 ( $\pm$ 0.46) <sup>E</sup>
<b>C<sub>4</sub></b>	88.77 ( $\pm$ 0.28) <sup>B</sup>	1334 ( $\pm$ 4) <sup>B</sup>	187.0 ( $\pm$ 2.4) <sup>G</sup>	71.92 ( $\pm$ 1.12) <sup>E</sup>	82.46 ( $\pm$ 0.44) <sup>D</sup>
<b>C<sub>5</sub></b>	16.48 ( $\pm$ 0.38) <sup>A</sup>	372.9 ( $\pm$ 2.9) <sup>A</sup>	24.44 ( $\pm$ 0.22) <sup>A</sup>	8.492 ( $\pm$ 0.11) <sup>A</sup>	12.05 (0.14) <sup>A</sup>

$F_1 - F_3$ : Freshly squeezed juices.  $F_3$  was obtained from pomegranate labeled as organic.  $C_1 - C_5$ : Commercial 100% pomegranate juices.  $Li^+$  was not detected in any of the samples.

\*Different letters (A, B, C, D, E, F, G) represent the Duncan group means ( $\alpha = 0.05$ ).

Findings in eight pomegranate juices samples ( $F_1 - F_3$ ,  $C_1 - C_5$ ) were analyzed and these samples were separately compared for the calculated amounts of each cation by using one-way ANOVA, followed by Duncan's multiple-range test. There was a significant difference between at least two of the samples' means according to the results of the one-way ANOVA ( $P < 0.05$ ). Duncan's test was used for doing multiple comparisons of eight

group means ( $F_1$ - $F_3$ ,  $C_1$ - $C_5$ ). The results obtained from this test are given in Table 4. These results indicate the significant difference between the most of the eight groups' means for five cations. However, as seen in Table 4, there was no statistically significant difference among the means of samples represented with same letter.

The LOD values for the cations were between about 2.0  $\mu\text{M}$  and 4.9  $\mu\text{M}$  except  $\text{Li}^+$  in this study. These values are similar or lower than the LOD previously reported for  $\text{C}^4\text{D}$  system. Opekar and Tůma designed a new CE apparatus for detection of some cations and anions, the LOD values were reported as 6.9 and 10.6  $\mu\text{M}$  in Krystalon fertilizer solution for  $\text{K}^+$  and  $\text{NH}_4^+$ , respectively.<sup>21</sup> Doung et al. also designed a homemade CE system for water analysis and the LOD values were found as 4.5, 5.0, 5.5, 6.0, and 10.0  $\mu\text{M}$  for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ , and  $\text{Na}^+$ , respectively.<sup>22</sup> Kubáň and Hauser developed a method using an external  $\text{C}^4\text{D}$  with microchip CE for the analysis of ions including metal cations in beverages and their LOD values were between 7.5  $\mu\text{M}$  and 13.6  $\mu\text{M}$  for metal cations including  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ , and  $\text{Na}^+$  in buffer solution consisting of 10.5 mM histidine, 50 mM acetic acid, and 2 mM 18-crown-6.<sup>23</sup> Mori et al. reported the LOD values of metal cations, namely  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$  ranging from 2.0 to 3.0  $\mu\text{M}$  where the background electrolyte was composed of both 30 mM lactic acid and histidine with 3 mM 18-crown-6.<sup>24</sup>

### 3.2. Conclusion

A rapid and economical method for quantification of the nutritive constituents in different pomegranate juices was achieved by CE- $\text{C}^4\text{D}$  method. The total analysis time for separation and quantification of six cations was accomplished in less than 4 min. The tested method offers a reliable analysis of cations found in pomegranate juices which includes potassium, magnesium, and sodium. These ions have significant effect on regulating blood pressure; thus, the amounts were analyzed in different pomegranate juices. The LOD values of the proposed method were lowered to  $\mu\text{M}$  levels. At the same time, high recovery, good linearity, and precision were obtained for the method. The amounts of these nutritive ions were successfully determined in both commercial and natural pomegranate juices.

## 4. Experimental

### 4.1. Reagents and solutions

Tris and MOPS were purchased from Sigma Aldrich (Steinheim, Germany). Inorganic salts of metal cations,  $\text{KNO}_3$ ,  $\text{NaCl}$ ,  $\text{LiCl}$ ,  $\text{NH}_4\text{Cl}$ , and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  were obtained from Merck (Darmstadt, Germany).  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  was obtained from J. T. Baker (New Jersey, USA). 18-crown-6 was purchased from Fluka (Buchs, Switzerland). All the other chemicals used were of analytical grade.

Stock solutions of cations were prepared by dissolving their salts in distilled water. Concentrations of stock solutions as ions were between 4.70 and 6.13 mM. They were stored in a laboratory refrigerator at 4 °C. Standard solutions of cations were freshly prepared from stock solutions at the beginning of each working day.

### 4.2. Preparation of samples from fruits and commercial juices

Three pomegranate fruits, one of which was organic, and five different commercial pomegranate juices which were labeled as 100% pomegranate juices were obtained from local markets. Pomegranate fruits were sliced and then squeezed with squeezing apparatus freshly and then sonicated for 15 min for degassing. The freshly squeezed fruit juices and commercial fruit juices were filtered through 0.22  $\mu\text{m}$  pore-sized microfilters and after the necessary dilutions, they were injected directly to the capillary column.

### 4.3. Instrumentation and working conditions

Separation of six inorganic cations was carried out with fused silica capillary obtained from Polymicro Technologies (Phoneix, USA) with 50 µm inner diameter. The total length of the column used was 80 cm and the effective length was 65 cm. On each working day, prior to the analysis, capillary was rinsed off with 1 M sodium hydroxide and water for 5 min and then running buffer solution was used for preconditioning of the capillary for 5 min. After every run of measurements, the capillary column was rinsed with 0.1 M NaOH, water, and buffer for 2 min to remove residues of sample matrix.

Separations were carried out with a commercial CE system by Prince Technologies coupled with TraceDec Contactless Conductivity Detector (BV, Emmen, the Netherlands). TraceDec contactless conductivity detector was set as 100% gain and -12 dB excitation voltage was applied to the first electrode. DAX 8.0 Data Acquisition and Analysis software (Van Mierlo Software Consultancy, Eindhoven, the Netherlands) was used for data processing. IBM SPSS 23.0 software (Chicago, IL, USA) was used as statistical analysis program for Windows. One-way ANOVA test was applied for the comparison of the significant differences between the pomegranate juices ( $P < 0.05$ ) based on mean values of cations calculated.

All the samples were injected from anodic side of the capillary under a 60 mbar pressure for 6 sec. The separation voltage was set constant during analysis at 20 kV. All the analysis procedures were carried out at 25 °C.

The composition of background electrolyte solution was 20 mM MOPS with 2.5 mM 18-crown-6 at pH of 7.5. All solutions were prepared in pure water obtained by Elga Purelab Option-7-15 (High Wycombe, UK) model system with 18.2 Ω resistivity.

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