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Research Article

Detection of Na^+, NH_4^+, K^+ and Ca^{2+} in the Yoghourt and Beer

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Abstract: Ion Chromatography (IC) has been developed for the determination of inorganic ions and organic acids. Chromatography can yield the precise and reproducible data if the experimental condition is kept constant. In this study, the cations Na^+, NH_4^+, K^+ and Ca^{2+} in the yoghourt and beers were determined with the technique of IC. A Dionex ICS-2000 ion chromatograph with a Dionex gradient pump, eluent degassing module and conductivity detector was used. Cations were separated on a CS12 A ion-exchange column, with a CG-12 A guard column and detected after suppression with CSRS 300 cation electrical self-regenerating suppressor. The results indicated that the technique of IC was suitable for the rapid, precise and accurate determination of Na^+, NH_4^+, K^+ and Ca^{2+} in the yoghourt and beer samples. In addition, the acceptable detection limits were obtained for Na^+, NH_4^+, K^+ and Ca^{2+} and the time of analysis was significantly shortened with the technique of IC. The data will provide theories and rapid methods for the supervision of yoghourt and beer quality.

Keywords: Beer, Ca^{2+}, ion chromatography, K^+, Na^+, NH_4^+, yoghourt

INTRODUCTION

Since the introduction of Ion Chromatography (IC) by Small *et al*. (1975), IC has been developed into the method of choice for the analysis of cations and anions in the water. IC has high precision and low maintenance costs and many parameters can be determined in one run with the technique of IC (Tartari *et al*., 1995; Marchetto *et al*., 1995; Rey and Pohl, 1996). The conductivity detectors combined with IC with chemical suppression is very suitable for the determination of inorganic ions and organic acids (Buldini *et al*., 1997a, b; Hafez *et al*., 1991) and the technique of IC has been widely used to analyze the quality of various waters (Ohta and Tanaka, 1999; Ding *et al*., 2001; Tanaka *et al*., 2001).

In the past, minor and trace elements, as well as some other water quality determinants, were mainly detected with the technique of analytical chemistry. The analytical chemistry techniques were used to ensure that the results were sufficiently reliable for the analysis of food quality. IC is a technique with high reliability and sensitivity for the determination of Group I and II cations and IC can simultaneously determinate all cations of interest plus ammonium ion in a shorter time with easy operation and sample preparation. Moreover, chromatography can yield the precise and reproducible data if the experimental condition is kept constant. The analysis of cations in food samples is important from the nutritional and toxicological point of view. In this study, the major cations Na^+, NH_4^+, K^+ and Ca^{2+} in the yoghourt and beer were determined with a Dionex ICS-2000 ion chromatograph.

MATERIALS AND METHODS

Instrument: A Dionex ICS-2000 ion chromatograph with a Dionex gradient pump, eluent degassing module and conductivity detector was used. Cations were separated on a CS12 A ion-exchange column (4 mm I.D.), with a CG-12 A guard column and detected after suppression with CSRS 300 (4 mm I.D.) cation electrical self-regenerating suppressor.

Reagents: All reagents, eluents and standard solutions were prepared using water purified with a Milli-Q system (Millipore). Na^+, K^+ and Ca^{2+} standard solutions (1000 mg/L, purchased from the standard solutions center in Shanghai) and NH_4^+ standard solutions (1814 mg/L, purchased from the standard solutions center in Shanghai) were used for cation determinations and methanesulphonic acid (Fluka) was used for preparation of cation determinations.

Treatment of real samples: The yoghourt and beers were purchased from a local market in zibo, Shandong province. For the ion chromatographic analysis, 2.0 mL acetic acid (5.0%) was added into 2.0 g yoghourt and centrifuged at 4000 r/min for 10 min. Then the supernatant was diluted twenty-five times with purified

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Table 1: Optimum condition for IC

Concentration of MSA	20 mmol/L
Flow rate of eluent	1.0 mL/min
The electric current of suppressor	59 mA
Chromatographic column	CS12 A ion-exchange column
Guard column	CG-12 A guard column

water. The samples of beers that contained carbon dioxide were ultrasonically degassed (10 min) to remove the bubbles and the beer was diluted 25 times with purified water. The final solutions of yoghourt and beers were filtered through 0.22 μm Nylon filters and Dionex on Guard C18 before analysis.

Cation chromatographic analysis: Isocratic elution was used for Na^+, NH_4^+, K^+ and Ca^{2+} determination with 20 mM Methanesulphonic Acid (MSA) as eluent (1.0 mL/min). The injection volume was 25 μL, the run time was set to 15 min.

RESULTS AND DISCUSSION

Determination of cations in the yoghourt:

Separation condition: The cations (Na^+, NH_4^+, K^+ and Ca^{2+}) were successfully separated by the optimum chromatographic conditions summarized in Table 1. Figure 1 shows the chromatogram of a standard solution. Chromatographic characteristics were also obtained: the theoretical plates for Na^+, NH_4^+, K^+ and Ca^{2+} were 4177, 3830, 4771 and 3288; the symmetry factors for the three analytes were 1.487, 1.596, 1.600 and 1.431, respectively; Na^+-NH_4^+ resolution was 2.004; NH_4^+-K^+ resolution was 3.600.

Linearity: Three standard solutions with increasing concentrations were used for calibration for Na^+, K^+, Ca^{2+} (1.0, 10.0 and 20.0 mg/L, respectively) and NH_4^+ (1.814, 18.14 and 36.28 mg/L, respectively) determinations. The calibration was linear for Na^+ ($y = 3.344x-0.358$; $r^2 = 0.996642$), NH_4^+ ($y = 7.246x$; $r^2 = 0.961018$), K^+ ($y = 5.128x - 0.179$; $r^2 = 0.998227$) and Ca^{2+} ($y = 2.564x - 0.251$; $r^2 = 0.998802$) (y is the amount of cations and x is the area of the chromatogram). The typical chromatogram obtained for Na^+, NH_4^+, K^+ and Ca^{2+} standard solutions are shown in Fig. 1.

Precision and detection limit: Under the optimum experiment conditions, the analytes all showed good linear relationship, sensitivity and reproducibility. Repeating five times, the precision of the analysis of one real sample was calculated. From Table 2, it can be seen that the Relative Standard Deviation (R.S.D.) for Na^+, NH_4^+, K^+ and Ca^{2+} ranges from 0.85 to 5.52%. The detection limit for the proposed method was calculated (3N/S) for cation determinations. The calculated detection limits for Na^+, NH_4^+, K^+ and Ca^{2+} were 0.897, 0.414, 0.585 and 1.17 μg/L, respectively.

Analysis of real samples: All the samples were pretreated according to the methods described and analyzed under the optimum conditions summarized in Table 1. The chromatogram of one of the real samples, yoghourt A, is shown in Fig. 2. The determination results of two kinds of yoghourt can be seen in Table 3.

Table 2: Precision and detection limit data for determination of cations

Sample	Na^+	NH_4^+	K^+	Ca^{2+}
R.S.D. (%) (n = 5)	4.160	5.520	0.850	1.56
Detection limit (μg/L)	0.897	0.414	0.585	1.17

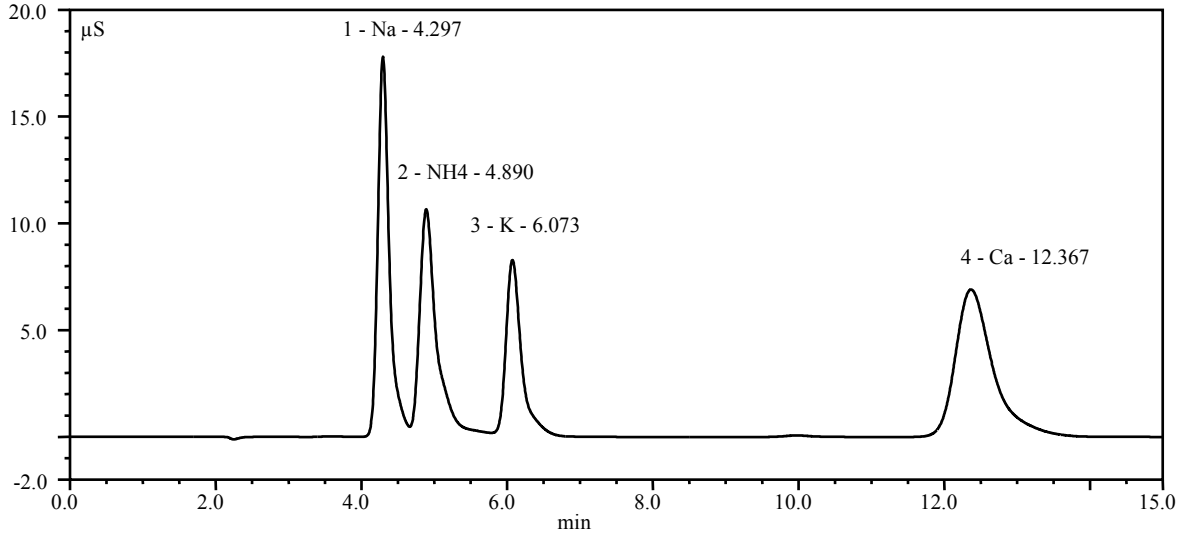

Fig. 1: The chromatogram for Na^+, K^+, Ca^{2+} standard solution (10.0 mg/L) and NH_4^+ standard solution (18.14 mg/L) Column: Dionex CS-12 A; Injection volume: 25 μL; Conductivity detector: Elution with 20 mM methanesulphonic acid

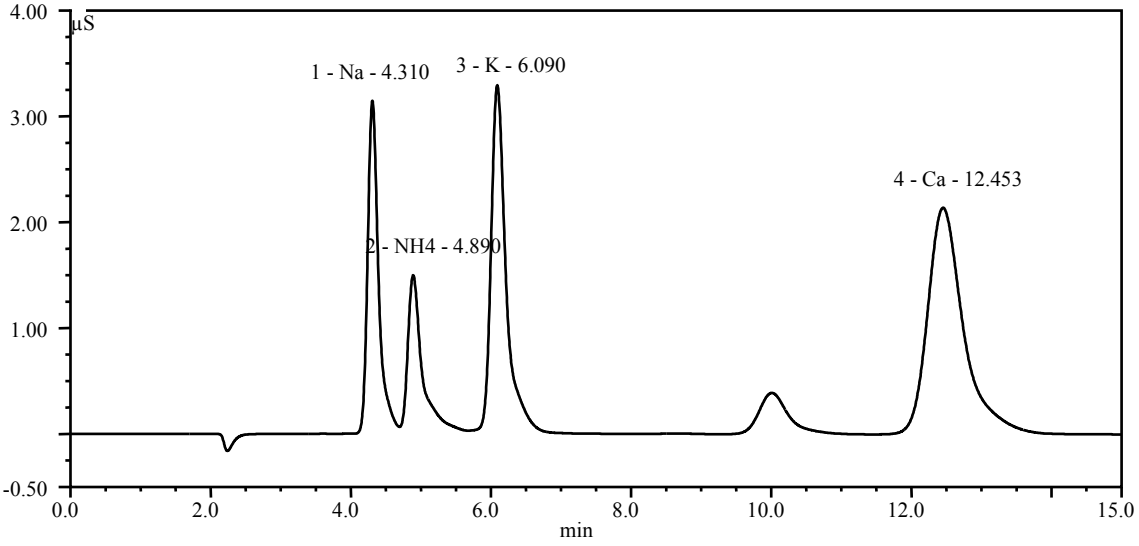

Fig. 2: The chromatogram for cations Na^+, NH_4^+, K^+ and Ca^{2+} in the yoghourt A
Column: Dionex CS-12 A; Injection volume: 25 μL; Conductivity detector: Elution with 20 mM methanesulphonic acid

Table 3: Analytical results and recovery data of Na^+, NH_4^+, K^+ and Ca^{2+} in the real samples

Samples	Na^+	NH_4^+	K^+	Ca^{2+}
Analytical results (n = 5)				
Yoghourt A (mg/g)	0.90±0.12	0.47±0.08	1.55±0.04	0.94±0.05
Yoghourt B (mg/g)	0.95±0.02	0.35±0.02	1.44±0.27	0.96±0.11
The recovery data (n = 3)				
Yoghourt A (%)	104.94±1.27	102.31±0.21	97.90±0.16	98.32±1.27
Yoghourt B (%)	96.85±1.14	106.26±0.56	103.29±0.39	98.46±0.57

Suitable amount of Na^+, NH_4^+, K^+ and Ca^{2+} standard solutions (5.0 mg/L of Na^+, K^+, Ca^{2+} and 9.07 mg/L NH_4^+) were added to the real yoghourt samples, the mixtures were analyzed using the proposed procedure. Recovery was expressed for each component as the mean percentage ratio between the measured amounts and the added ones. As shown in Table 3, the recovery data can be obtained for all the parameters, recoveries ranging from 96.85±1.14 to 106.26±0.56%.

Determination of cations in the beers:

Separation condition: The optimum chromatographic conditions were as the determination of cations in the yoghourt (Table 1). Chromatographic characteristics were also obtained: the theoretical plates for Na^+, NH_4^+, K^+ and Ca^{2+} were 3897, 3511, 4413 and 3108; the symmetry factors for the three analytes were 1.547, 1.621, 1.616 and 1.455, respectively; Na^+-NH_4^+ resolution was 1.939; NH_4^+-K^+ resolution was 3.509.

Linearity: Three standard solutions with increasing concentrations were used for calibration for Na^+, K^+, Ca^{2+} (1.0, 10.0 and 20.0 mg/L, respectively) and NH_4^+ (1.814, 18.14 and 36.28 mg/L, respectively) determinations. The calibration was linear for Na^+ ($y = 3.4981x + 0.0098$; $r^2 = 0.9994$), NH_4^+ ($y = 4.3674x - 1.5393$; $r^2 = 0.9918$), K^+ ($y = 5.1684x + 0.187$; $r^2 = 0.9991$) and Ca^{2+} ($y = 2.4583x + 0.3637$; $r^2 = 0.9972$).

Table 4: Precision and detection limit data for determination of cations

Sample	Na^+	NH_4^+	K^+	Ca^{2+}
R.S.D (%) (n = 5)	6.72	7.94	1.66	2.41
Detection limit (μg/mL)	0.86	0.69	0.58	1.22

Precision and detection limit: Under the optimum experiment conditions, the analytes all showed good linear relationship, sensitivity and reproducibility. Repeating five times, the precision of the analysis of one real sample was calculated. From Table 4, it can be seen that the Relative Standard Deviation (R.S.D.) for Na^+, NH_4^+, K^+ and Ca^{2+} ranges from 1.66 to 6.72%. The detection limit for the proposed method was calculated (3N/S) for cation determinations. The calculated detection limits for Na^+, NH_4^+, K^+ and Ca^{2+} were 0.86, 0.69, 0.58 and 1.22 μg/mL, respectively.

Analysis of real samples: All the samples were pretreated according to the methods described and analyzed under the optimum conditions. The chromatogram of one of the real samples, beer A, is shown in Fig. 3. The determination results of four kinds of beers can be seen in Table 5. Suitable amount of Na^+, NH_4^+, K^+ and Ca^{2+} standard solutions (5.0 μg/mL of Na^+, K^+, Ca^{2+} and 9.07 μg/mL NH_4^+) were added to the real beer samples, the mixtures were analyzed using the proposed procedure. Recovery was expressed for each component as the mean percentage ratio between the

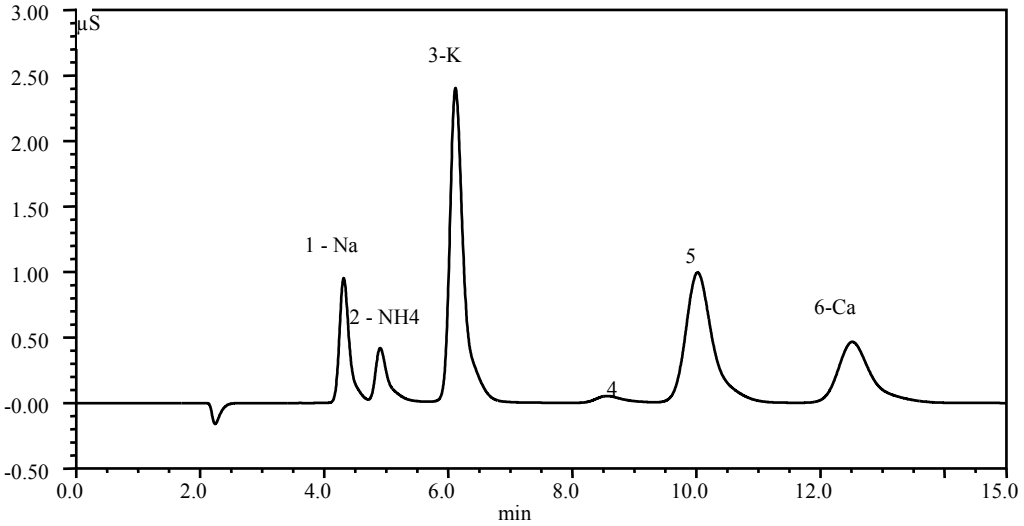

Fig. 3: The chromatogram for cations Na^+, NH_4^+, K^+ and Ca^{2+} in the beer A
Column: Dionex CS-12 A; Injection volume: 25 μL; Conductivity detector: Elution with 20 mM methanesulphonic acid

Table 5: Analytical results and recovery data of Na^+, NH_4^+, K^+ and Ca^{2+} in the real samples

Samples	Na^+	NH_4^+	K^+	Ca^{2+}
Analytical results (n = 5)				
Beer A (mg/L)	65.26±0.18	22.33±0.07	233.82±0.16	37.12±0.04
Beer B (mg/L)	54.91±0.48	21.12±0.10	165.72±0.35	63.68±0.09
Beer C (mg/L)	58.52±0.13	89.28±0.22	355.17±0.22	34.96±0.04
Beer D (mg/L)	48.88±0.78	48.24±0.12	181.45±0.43	45.91±0.16
The recovery data (n = 3)				
Beer A (%)	108.94±1.67	104.31±0.31	107.90±1.16	96.52±2.27
Beer B (%)	97.95±5.13	108.56±0.66	107.29±3.39	98.38±1.37
Beer C (%)	98.50±7.38	98.17±0.86	102.92±5.58	107.68±6.28
Beer D (%)	103.46±6.26	107.00±1.06	105.12±4.30	108.34±5.86

measured amounts and the added ones. As shown in Table 5, the recovery data can be obtained for all the parameters, recoveries ranging from 96.52±2.27 to 108.94±1.67%.

CONCLUSION

IC has been developed for the determination of inorganic ions and organic acids. Chromatography can yield the precise and reproducible data if the experimental condition is kept constant. In this study, the cations Na^+, NH_4^+, K^+ and Ca^{2+} in the yoghourt and beers were determined with the technique of IC. The results indicated that the technique of IC was suitable for the rapid, precise and accurate determination of Na^+, NH_4^+, K^+ and Ca^{2+} in the yoghourt and beer samples and IC can be used to provide suitable parameters for discrimination among different types of yoghourt and beer. The analytical method proposed showed a high sensitivity and reproducibility and has the advantage of quantifying the cations in the yoghourt and beer. IC offers a wide dynamic range and allows the simultaneous determination of all cations of interest plus ammonium ion in less than 15 min. In addition, the acceptable detection limits were obtained for Na^+, NH_4^+, K^+ and Ca^{2+} and the time of analysis was significantly shortened with the technique of IC.

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