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Determination of ion species within commercial beverages utilizing fast ion chromatography

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ABSTRACT

Ion species present in various popular commercial beverages were successfully determined by ion chromatography. Ions identified with solvent conditions utilized included Na^{+}, H_4^{+}, K^{+}, Ca^{2+}, Mg^{2+}, PO_4^{3-}, SO_4^{2-}, and Cl^{1-}. Beverages analyzed included popular types of wheat beer, non-wheat beer, mescato white wine, concord grape red wine, green tea, herbal tea, vitamin waters, fruit juices (ie. cranberry, orange pineapple, etc) and various flavored waters. All samples were injected without dilution but clarified and kept sterile. The solvent system utilized here successfully separated ions from aliquot injected without problems within the column and conductivity detector. All alcoholic beverages showed Cl^{1}, Mg^{2+}, Ca^{2+} and K^{+}; with wheat beer and mescato white wine showing these ions as well as both Na^{+} and NH_4^{+}. Flavored waters (ie. cherry, tangerine lime, strawberry) showed various cations and anions with significant variation of quantity and types. Likewise, commercial teas and fruit juices showed substantial variations in types and quantities of ionic species detected. Several example ion chromatograms are presented and show clearly the overall excellent resolution of species peaks obtained with this solvent system and instrument parameters. Therefore a broad variety of commercial beverages were analyzed by ion chromatography producing well elucidated chromatogram peaks and identification of cations and anions important in nutrition. These parameters should allow effective analysis of a broad assortment of food products for nutrition appraisal.

KEYWORDS

Ion chromatography;
Beverages;
Cation;
Anion.

INTRODUCTION

Ion chromatography refers to the modern method of chromatographic separation of cations and anions[1]. Although dilution of samples is very common, researchers pursue experimental parameters permitting straight or non-treated sample injection[1]. Major requirements of system parameters include the following: 1) Efficient exchange columns with maximal number of plates; 2) Elution approach permitting resolution of retention times; 3) Rapid achievement of equilibrium so that peak broadening is minimized; 4) Convenient elution time; and 5) Eluent and resin compatible with the detection system[1]. Ion chromatography analysis is applied to food and beverage analysis, pharmaceuticals, waters analysis, petrochemical, and other industries[1-3].

Speciation elucidation of nitrogen in water samples is an important category of environmental studies, with ion chromatography an effective approach for determination of nitrogen species NO_2^{1-}, NO_3^{1-}, and NH_4^{+1}[4]. Other studies have also substantiated the efficacy of ion chromatography for identification of anthropogenic sources of nitrates and related species emitted from municipal and industrial wastes[5]. In addition, ion chromatography has found highly efficacious application in food analysis for therapeutic nutrition, athletic programs, and compliance with legal standards[6-8].

Ion chromatography has been shown to identify and quantify EDTA in canned foods as well as pharmaceuticals[9]. Total nitrogen content of foods and environmental samples can be effectively quantified by ion chromatography following Kjeldahl digestion[10]. Ion chromatography with ultraviolet detection can simultaneously determine hypophospite, phosphate, chlorides, nitrate, sulfate, and orthophosphates[11]. Other studies have demonstrated analysis by single column for nitrate and chloride ions[12], phytic acid[13], chloride in mustard sauces[14], bromide ions[15], free and total sulfites[16]. Presented here are instrumental parameters suitable for commercial beverage analysis.

EXPERIMENTAL

Reagents and instrumentation

All reagents were acquired from Sigma-Aldrich Company (Sigma-Aldrich, P.O. Box 2060, Milwaukee, WI 53201 USA). For the reagents necessary to operate the single column Metrohm 792 Basic IC instrument, then 18 mOHM water was utilized as solvent. For cation analysis a Metrosep Cation 1-2 column (size 7.0 μm, pressure 6.5 MPa, cond 829.2 μS/cm) was used with eluent 0.1 M H_2SO_4, 0.002 M HNO_3, and 0.00075 M 2,6-pyridinedicarboxylic acid in 18 mOHM water. For anion analysis a ICSep AN1 column (size 10μm, pressure 6.8 MPa, cond 12.9μS/cm) was used with eluent 0.1 M H_2SO_4, 0.0018 M Na_2CO_3, and 0.0017 M $NaHCO_3$ in 18 mOHM water. Ion detection was accomplished by conductivity.

Commercial samples for analysis

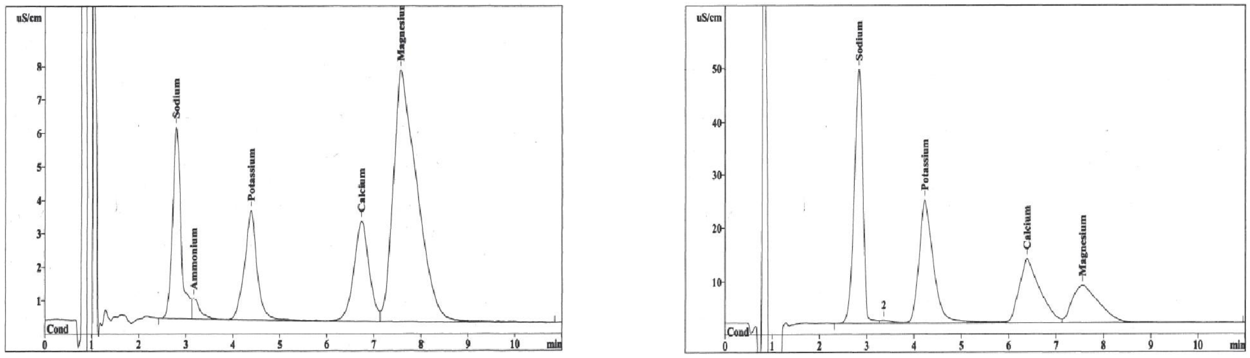
Various examples of commercial beverages were obtained for analysis which included: flavored waters (ie. cherry, strawberry, etc), fruit juices (ie. cranberry, mango, etc) and mixtures of fruit juices (ie. orange pineapple, cranberry-grape, etc), teas (ie. green, herbal, etc), vitamin waters, and alcoholic liquors (ie. Wheat beer, non-wheat beer, red wine, white wine). Aliquots of beverages were placed into sterile tubes (FALCON, Becton Dickinson Labware, Franklin Lakes, NJ 07417) and stored at 4°C until analysis. Samples for analysis were injected onto columns for analysis without dilution.

RESULTS AND DISCUSSION

The chemical composition and physical properties of foods are utilized to evaluate the nutritive value[17]. Food analysis is a part of food quality assurance and has various driving factors including the following: 1) Customer expectations of a nutritive and safe food; 2) Environmental concerns (concerns for safety of environment); 3) Organic foods (more demands for organic food); 4) Technology (new process and methods of food development have emerged); 5) Regulatory requirements (stringent safety and quality demands)[17].

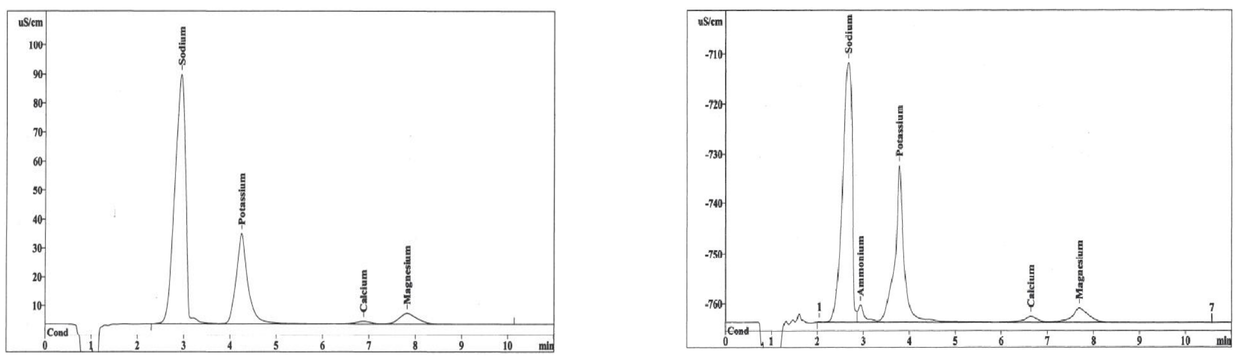
Minerals in diet have a nutritional and functional importance that necessitates the control and knowledge of their levels[17]. Some foods are fortified with minerals to increased concentrations above the natural level and thereby required monitoring[17]. The minerals calcium, phosphorus, sodium, potassium, magnesium, sulfur, and chloride are dietary macro minerals, of which an adult requires more than 100 milligrams each per day[17]. In addition, there are 10 trace minerals required at milli- or microgram levels each day[17], and include iron, iodine, zinc, copper, chromium, manganese, molybdenum, fluoride, selenium, and silica. Necessary minerals essential roles in biological action within the body. However, some minerals are toxic in the body, should be avoided, and include lead, mercury, cadmium, and aluminum[17].

The National Academy of Sciences has determined a recommended dietary allowance of minerals for both male and female which include the following (male/female requirement): calcium (1000 mg/1200 mg), sodium (1100 mg/3300 mg), potassium (2000 mg/2000 mg), iron (10 mg/15 mg), magnesium (350 mg/280 mg), phosphorus (800 mg/1200 mg), chlorine (700 mg/700



Cation chromatogram of vitamin water **Cation chromatogram of cranberry juice**

Figure 1 : A chromatogram of example vitamin water shows Na^+, NH_4^+, K^+, Ca^{2+}, and Mg^{2+} at 2.79 min, 3.17 min, 4.39 min, 6.74 min, and 7.57 min, respectively. The example chromatogram of cranberry fruit juice shows Na^+, K^+, Ca^{2+}, and Mg^{2+} at 2.84 min, 4.23 min, 6.39 min, and 7.56 min, respectively



Cation chromatogram of herbal tea **Cation chromatogram of green tea**

Figure 2 : Chromatogram of example herbal tea shows Na^+, K^+, Ca^{2+}, and Mg^{2+} at 2.95 min, 4.25 min, 6.88 min, and 7.82 min, respectively. Example of commercial green tea 2-way chromatogram shows Na^+, NH_4^+, K^+, Ca^{2+}, and Mg^{2+} at 2.68 min, 2.94 min, 3.78 min, 6.64 min, and 7.69 min, respectively

mg), copper (2 mg/2 mg), and chromium (0.2 mg/0.2 mg)[18].

Therefore, commercial beverages have been analyzed by ion chromatography for content of the following cations and anions: Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, PO_4^{3-}, SO_4^{2} and Cl^{1-}. Example chromatograms for vitamin water and cranberry juice are presented in figure 1. All samples were injected without dilution and for these beverages pre-clarification was done by the manufacturer, so filtering by gravity filtration was not necessary, which accelerates the speed and efficacy of analysis.

Chromatograms provide a 2-way plot of the elution profile from column discharge as a plot of time (minutes) as the independent variable versus microSiemens per centimeter (μS/cm) as the dependent variable (where Siemens is a unit of electrical conductivity). The top chromatogram presented in figure 1 introduces the example vitamin water showing Na^+, NH_4^+, K^+, Ca^{2+}, and Mg^{2+} at 2.79 min, 3.17 min, 4.39 min, 6.74 min, and 7.57 min, respectively. The bottom chromatogram present example cranberry juice showing Na^+, K^+, Ca^{2+}, and Mg^{2+} at 2.84 min, 4.23 min, 6.39 min, and 7.56 min, respectively. The peaks are identifiable and can be utilized for quantization of ions when converting to parts per million. Note that sodium, potassium, calcium, magnesium are macro nutrient minerals and required nutrition. From food analysis the consumer can monitor value of beverage for supplying desired macro minerals as nutrition as well as for medicinal consideration such as for blood pressure and cardiovascular retrospection.

The top chromatogram presented in figure 2 introduces the example herbal water showing Na^+, K^+, Ca^{2+} and Mg^{2+} at 2.95 min, 4.25 min, 6.88 min, and 7.82 min, respectively. A commercial green tea 2-way chromatogram (see Figure 2, bottom chromatogram) shows

TABLE 1 : Cations and anions found in commercial flavored waters

Sample type	Molarity							
	Na^+	NH_4^+	K^+	Ca^+	Mg^+	PO_4^{3-}	SO_4^{2-}	Cl^-
Cherry water	4.42E-4	2.44E-4	4.33E-3	1.74E-4	6.03E-4	3.21E-6	ND	ND
Black cherry water	2.38E-4	1.25E-4	5.62E-3	ND	4.56E-4	ND	1.49E-4	ND
Tangerine lime water	ND	ND	1.47E-4	ND	1.03E-5	3.78E-4	7.02E-5	1.40E-4
Strawberry water	ND	ND	1.30E-5	ND	ND	ND	8.34E-5	ND

ND=not detected

TABLE 2 : Cations and anions in commercial vitamin waters

Sample type	Molarity							
	Na^+	NH_4^+	K^+	Ca^+	Mg^+	PO_4^{3-}	SO_4^{2-}	Cl^-
Peach plus calcium	4.43E-4	ND	1.12E-3	2.68E-2	ND	ND	ND	1.17E-2
Lemonade	3.92E-4	ND	1.42E-3	3.86E-3	6.76E-3	ND	7.60E-4	1.24E-2
Pomegranate	3.47E-4	1.98E-5	2.68E-4	2.09E-4	4.88E-4	1.15E-6	ND	ND

ND=not detected

TABLE 3 : Cations and anions of commercial fruit juices

Sample type	Molarity							
	Na^+	NH_4^+	K^+	Ca^+	Mg^+	PO_4^{3-}	SO_4^{2-}	Cl^-
Orange pineapple	ND	ND	6.62E-6	ND	1.73E-5	ND	ND	2.42E-5
Cranberry grape	3.58E-5	ND	8.95E-6	3.03E-5	6.82E-6	ND	ND	1.95E-4
Cranberry	2.88E-3	ND	5.77E-3	1.10E-3	3.24E-4	ND	7.89E-5	8.72E-5
Nectar (Strawberry- mango)	6.47E-3	2.35E-4	5.70E-3	1.26E-3	1.97E-3	1.15E-6	ND	4.49E-5
Nectar (Mango)	4.02E-3	ND	1.13E-3	2.61E-3	1.35E-4	ND	ND	3.09E-4

ND=not detected

Na^+, NH_4^+, K^+, Ca^{2+}, and Mg^{2+} at 2.68 min, 2.94 min, 3.78 min, 6.64 min, and 7.69 min, respectively. The peaks are identifiable and can be utilized for quantization of ions when converting to parts per million. Note that sodium, potassium, calcium, magnesium are macro nutrient minerals and required nutrition.

Knowing the type and concentration of specific minerals in food beverages is important in the food industry. Some physicochemical properties of minerals that endue the identification and measure concentration are: 1) Low volatility; 2) Unique electromagnetic spectra; 3) Reactivity with reagents to produce measurable change. Here, elution of ions is monitored by conductivity measurement. Outcome of ion chromatography analysis of commercial flavored waters is presented in TABLE 1. No example water showed all ions that were monitored (ND = not detected). For cations, potassium was found in all samples at molarities ranging from 1.30E-5 molar to 5.62E-3 molar. Calcium cation was found only in cherry water and chloride anion was found only in tangerine lime water.

Commercial vitamin waters are quite popular and widely available for consumption. Three variants of vitamin water analyzed (see TABLE 2) showed that sodium, potassium, and calcium are present in all samples. Sodium, potassium, and calcium are macro nutrients and define the popularity of these beverages among athletes. Ions of ammonium, phosphate, and sulfate are found only in pomegranate and lemonade type, respectively. Previous studies have shown that potassium has a modest blood pressure lowering effect in individuals having a low dietary intake[19]. Magnesium plays a role in various types of chronic, disease related conditions[20], and magnesium has a major role in regulation of blood pressure[20]. Although all data pertaining to use of magnesium is inconsistent, it does appear that magnesium intake reduces blood pressure is strongest when obtained from food rather than supplements[20]. Researchers have shown that a combination of vitamins and minerals can effectively reduce blood pressure for type 2

TABLE 4 : Cations and anions in commercial tea

Sample type	Molarity							
	Na^+	NH_4^+	K^+	Ca^+	Mg^+	PO_4^{3-}	SO_4^{2-}	Cl^-
Herbal tea (Ginseng-Valerian)	6.63E-3	ND	7.03E-3	7.43E-5	1.43E-4	ND	1.81E-4	ND
Green tea	5.50E-3	1.85E-4	2.27E-3	9.62E-5	2.38E-4	4.30E-5	1.83E-4	1.20E-4
Peach & green tea	4.82E-5	ND	5.81E-6	ND	1.21E-5	ND	ND	1.15E-4
Ginseng-Honey Green tea	8.74E-6	ND	ND	8.83E-6	1.32E-6	8.87E-5	8.19E-5	ND

ND=not detected

TABLE 5 : Cations and anions in commercial alcoholic beverages

Sample type	Molarity							
	Na^+	NH_4^+	K^+	Ca^+	Mg^+	PO_4^{3-}	SO_4^{2-}	Cl^-
Wheat beer	2.21E-3	1.53E-2	3.95E-2	4.24E-4	6.50E-3	ND	ND	2.98E-3
Non-Wheat beer	ND	ND	2.35E-6	2.07E-5	2.57E-5	1.15E-6	6.92E-5	1.01E-4
Concord grap-red beer	1.84E-5	ND	1.30E-5	6.32E-5	1.22E-4	ND	9.14E-5	1.51E-3
Moscato white wine	2.04E-5	7.10E-6	2.99E-5	5.11E-5	1.98E-5	ND	ND	2.73E-3

ND=not detected

diabetic patients[21].

Fruit juices are well known for beneficial vitamin content, but they also can be a source of minerals. Outcome results for fruit juice analysis is presented in TABLE 3 for well known examples of cranberry juice, nectars (strawberry-mango and mango), and ubiquitous combination such as orange-pineapple and cranberry-grape. Cations potassium and magnesium are found in all examples here with ammonium (NH_4^+) appearing only in strawberry-mango nectar. Sodium and calcium appear in all fruit juice examples except orange-pineapple. For anions, chloride ion appears in all samples with phosphate (PO_4^{3-}) and sulfate (SO_4^{2-}) appearing only in strawberry-mango nectar and cranberry juice, respectively.

Much publicity has been given to green tea for its potential in lending substantial benefits from consumption as a brewed tea. Various studies have shown that the consumption of green tea accompanying intake of mushrooms can reduce the risk of breast cancer[22]. In addition, another study has shown that green tea consumption with tamoxifen is effective against breast cancer[23]. Some work has been completed that reveals there are multiple targets for prostrate cancer chemoprevention that are amenable to green tea application[24]. Other studies have corroborated the potential for green tea consumption to decrease the rish of advance prostrate cancer[25]. Commercial teas where analyzed and results for ion identification is presented in TABLE 4, showing one herbal tea and three green tea beverages. Sodium and magnesium cations were found in all examples at varying concentrations, with ammonium (NH_4^+) identified in only straight green tea sample. Potassium was found in herbal tea, straight green tea, and peach flavored green tea. Sulfate anion (SO_4^{2-}) was found in herbal tea, straight green tea, and ginseng-honey green tea. Chloride anion was identified in straight green tea and peach flavored green tea.

Alcohol beverages are widely consumed and are shown in this study to have a number of macro mineral nutrients such as sodium, potassium, calcium, and magnesium, with sulfur in the form of sulfate (see TABLE 5). Interestingly calcium, potassium, magnesium, and chloride were found in all examples: wheat beer, non-wheat beer, Concord grape red wine, and moscato white wine. Sulfur in the form of sulfate was found in non-wheat beer and Concord grape red wine. The anion phosphate (PO_4^{3-}) was found only in non-wheat beer. Sodium was identified in wheat beer, Concord grape red wine, and moscato white wine. Some studies have shown that the consumption of alcoholic beverages have proven a substantial portion of the ability to reduce the risk of heart disease is linked to the alcohol content[26]. These findings in accompanying other studies of nutrients in alcoholic beverages will assist in determining the overall health benefits/loss of consumption of commercially available alcoholic beverages.

CONCLUSION

Ion chromatography effectively separated and identified various cations and anions in commercial beverages, including two types of beers and wines. Flavored waters and vitamin waters showed Na^{+}, NH_4^{+}, K^{+}, Ca^{2+}, Mg^{2+}, PO_4^{3-}, SO_4^{2-}, and Cl^{1-} to various concentrations but not confluent across the many samples that were analyzed. For fruit juices cations K^{+} and Mg^{2+} were found in all juices as was chloride anion, whereas other ions varied in presence and concentration. Commercial teas analyzed varied in presence and concentration of cations and anions. For alcoholic beverages analyzed (wheat beer, non-wheat beer, concord red wine, moscato white wine) K^{+}, Ca^{2+}, Mg^{2+}, and Cl^{1-} was found in all samples, whereas other ions varied in presence and concentration. Ion chromatography at the parameters here revealed information of commercial beverages useful for nutrition appraisal.

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