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Identification and relative ratios of cations and anions in orange juice, banana, soft drink, and various mineral tablets

Ronald Bartzatt*, Kelsey Palm, Nancy Handler

University of Nebraska, College of Arts & Sciences, Durham Science Center, Chemistry Department, 6001 Dodge Street, Omaha, Nebraska-68182, (USA)

E-mail : rbartzatt@mail.unomaha.edu

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ABSTRACT

The identification and determination of relative ratios of cations and anions in various food products were determined by ion chromatography. All samples studied were fresh and intact from the commercial containers. Where appropriate the samples were diluted in distilled water before injection into a Metrohm 792 instrument with distilled water to reduce potential background effects of non-ionic components. Cations identified in orange juice and include sodium, potassium, calcium, and magnesium, having relative ratios of 1.88:119.6:1:2.2, respectively. For diet coke the cations identified included sodium, ammonium, potassium, calcium, and magnesium having relative amount ratios of 7.84:5.19:14.6:5.41:1, respectively. Potassium was the predominant species identified in potassium citrate tablets and calcium is the major ion isolated from calcium carbonate antacid tablets. Potassium is predominant after distilled water extraction of fresh banana, followed by magnesium, calcium, sodium, and ammonium, where the relative amount ratios were 248.9:25.2:14.7:2.08:1, respectively. Anions discerned in banana included chloride, phosphate, and nitrate. Cations identified in powerade zero included sodium potassium, calcium, and magnesium, while anions included chloride, phosphate, and sulfate. A sample of Gatorade G-2 was analyzed and cations sodium and potassium were predominant, while anions observed included chloride, phosphate, and sulfate. The analysis of food materials by ion chromatography reveal useful information pertaining to the nutritional relevance of specific commercial products.

KEYWORDS

Ion chromatography;
Cations;
Anions.

INTRODUCTION

Ion chromatography (IC) is an indispensable tool of analytical chemistry[1]. Separation of complex mixtures of anions and cations can be achieved for identification and determination[1]. Inorganic ions and even larger organic ions can be identified by IC when utilizing columns packed with solid ion-exchange material. These types of analysis reach into many branches of physical sciences[1]. The capability to identify multiple ion species with a single sample injection is powerful characteristic of ion chromatography.

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Whereas the types and amount of ions are a issue for dietary nutritionists the application of IC enables better understanding of the nutritional value of food preparations. With the application of judicious approaches to sample preparation it has been possible to determine inorganic ions in food[2]. Manufacturers may have specific parameters to follow in order to adhere to governmental requirements or simply quality of product. Presence and amount of chloride anion in mustard sauces can be effectively monitored by using a suitable eluent system with ion chromatography[3]. Other studies have determined bromide ions using microwave digestion followed by ion chromatography with non-suppressed conductivity detection[4]. Single column IC has been shown previously to effectively separate and identify nitrate and chloride anions derived from the same food sample[5].

A method to detect free and total sulfites in food has been developed by use of ion chromatography utilizing electrochemical detection[6]. Ion chromatography can be used to detect phytic acid in soy flour, soy isolate, wheat bran, wheat bread, and infant formula powder[7]. The EDTA concentration of various matrixes such as synthetic drug injection drug solutions, contact lens solutions, canned mayonnaise, and canned mushrooms can be determined in the presence of interfering analogous compounds, such as EGTA, utilizing ion chromatography coupled with suppressed conductivity detection[8].

More complex analytes have been successfully determined using ion chromatography. These include stinging insects vespid venoms[9] and various proteins[10,11]. This work presents the ion chromatography analysis of various athlete orientated beverages, various mineral tablets, as well as soft drinks, banana, and orange juice. The relative amounts of ions present can be determined, providing greater knowledge of the actual nutrient capability of these commercial products.

EXPERIMENTAL

Reagents and instrumentation

All reagents were acquired from Sigma-Aldrich Company (Sigma-Aldrich, P.O. Box 2060, Milwaukee, WI 53201 USA). Where further treatment of commercial products was necessary (ie. dilution, solubilization, mixing, etc) then distilled water was utilized. For the reagents necessary to operate the single column Metrohm 792 Basic IC, 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 10 μm, pressure 6.8 MPa, cond 12.9 μS/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. Detection was accomplished by non-suppressed conductivity.

Preparation of liquid samples

Diet coke was injected undiluted into the instrument with no dilution. Orange juice

Obtain 10.00 mL of juice and dilute to a total volume of 200.00 mL using distilled water, then inject. Gatorade G-2: Take 10.00 mL of sample and dilute to 50.00 mL with distilled water then inject. Powerade Zero: Obtain 10.00 mL of sample and dilute to 50.00 mL total volume using distilled water, followed by injection into instrument.

Preparation of solid samples

For fresh banana material, a 65.958 gram amount was placed into a 200.00 mL volumetric flask then distilled water added to volume, followed by mixing by inversion for a period of 50 minutes. After which the liquid was filtered through Whatman #1 paper to separate the solid material from the collected filtrate that was then injected. Dissolve potassium citrate tablet portion of 0.052 grams, taken from a total mass of 0.541 grams, into a total volume of 100.00 mL of distilled water, which is then followed by injection. For the calcium carbonate antacid tablet, a 0.072 gram portion was taken from a total mass of 1.346 gram tablet, dissolved into 100.00 mL of distilled water, followed by injection.

RESULTS AND DISCUSSION

Food products are analyzed to meet compliance with labeling and legal requirements, establish nutritive value, determine product quality, and identify defects,

research and development. This information is vital for economically producing safe and nutritious food. Medical studies have shown that judicious choices for food consumption can help deter adverse reactions to food allergies and food sensitivities. Nutrition can play a role in carcinogenesis as well as aggravate conditions of diabetes, digestive disease, eating disorders, heart health, osteoporosis, weight, and obesity. Knowledge of the type and concentration of specific minerals found in food products is important to the food industry. Ion chromatography is known to be an effective tool in identifying many types of cations and anions[12,13], this work focuses on water soluble ions that are readily available in common products. In addition this analysis establishes the relative ratio of these ion species, this being information useful for deciding the nutritive potential for dietary needs.

A regular orange juice product was obtained and 10.00 mL diluted quantitatively to 200.00 mL with distilled water prior to injection. This product was enhanced with potassium which indeed appeared dominant on the chromatogram presented in figure 1. Taking into account the dilution step the potassium appears to be 0.115 molar in this orange juice. The ratio of sodium, potassium, calcium, and magnesium by concentration was determined to be 1.88:119.6:1:2.2, respectively. Therefore for this orange juice the potassium was a major component and in greater amounts than sodium, calcium, and magnesium. Concentrations of calcium, sodium, and magnesium are determined to be 0.000941 M, 0.00309 M, and 0.00339 M, respectively. This orange juice could be applied as a significant source of nutritive potassium. Anions identified in this orange juice included chloride, phosphate, and sulfate in relative ratios of 1:17.2:3.6, respectively.

The dominant phosphate is determined to be at a concentration of 0.0143 M. Therefore this analysis will be useful for dieticians requiring these minerals for patient treatment. The diet coke sample was injected directly into the instrument and did not require dilution steps. Various monovalent and divalent ions were identified and shown in figure 2. Within diet coke and eluting in the following order are sodium, ammonium, potassium, calcium, and magnesium at relative ratios (based on amounts per liter estimated by instrument) 7.84 :5.19: 14.6 : 5.41 : 1, respectively. Potassium is at the highest amount within this soft drink based upon mass per liter. Anions identified in undiluted diet coke eluted in order, chloride, phosphate, and sulfate, respectively (Figure 1). The anions present in ratio, by mass per liter, as 1:4.26:2.49, respectively. Therefore the amount of salts present in this soft drink may require consideration if dietary limitations or personal health issues are significant.

Potassium is utilized clinically as a diuretic[14] and is a major cation within cells. Deficiency in potassium can be manifested by impaired neuromuscular function, changes in gastric secretion, myocardium abnormalities such as conduction defects and disturbed ECG patterns, and abnormal functioning of the kidney[14]. Potassium supplements can be found in the form of potassium citrate tablets ($C_6H_5K_3O_7$, molar mass = 306.395 grams/mole) that are soluble in water. Excessive potassium consumption runs the risk of cardiotoxicity[14]. An analysis of a commercial potassium citrate tablet was achieved by grinding the tablet first in a mortar and pestle followed by selection of a known mass of 0.052 grams from a total mass of 0.541 grams and that amount dissolved into final volume of 100.00 mL of distilled water. The cations identified are shown in figure 3 and include in order of elution, sodium, ammonium, potassium, and calcium. The relative ratio of these cations by mass per liter where determined to be 2.56:1 : 163.0:24.6, respectively. Clearly and as expected the potassium species is dominant relative to other cations.

Calcium is present in small quantities within extracellular fluid and is the fifth most abundant element in the body[14]. Calcium plays important physiological roles, being essential for function of the nervous and muscular systems, and is necessary for normal cardiac function[14]. Over 90% of calcium within the body is found in the skeleton in the form of phosphates and carbonates[14], albeit that calcium is in constant exchange with the calcium of the interstitial fluids[14]. Calcium carbonate has a large neutralizing capacity and it is an excellent antacid, having rapid onset and prolonged duration[14], but inducing acid rebound. An over the counter calcium carbonate antacid tablet was ground by mortar and pestle followed by a 0.072 gram portion taken from a total mass of 1.346 gram tablet and dissolved into 100.00 mL of distilled water, then injected. As anticipated the calcium ion is the dominant ion compared to

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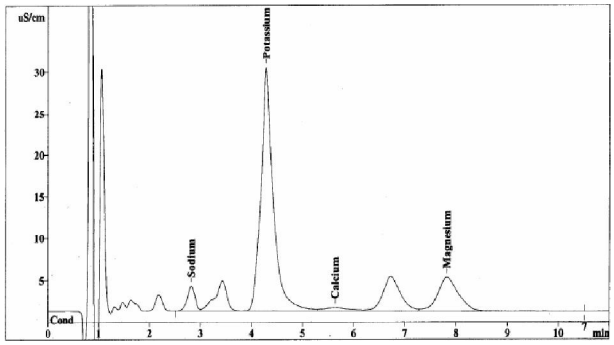
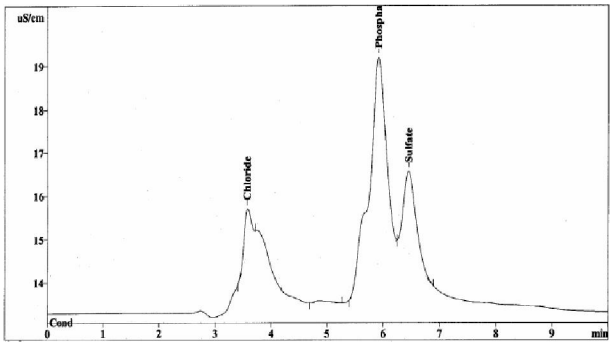
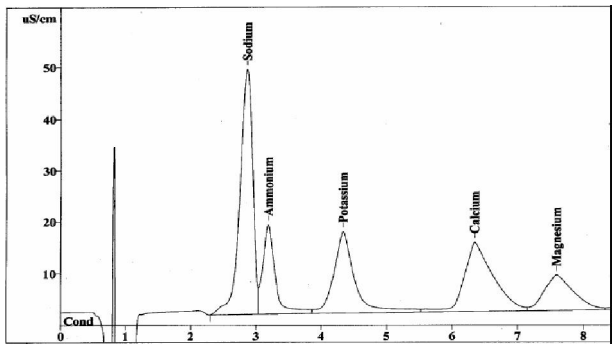


Cations identified in orange juice

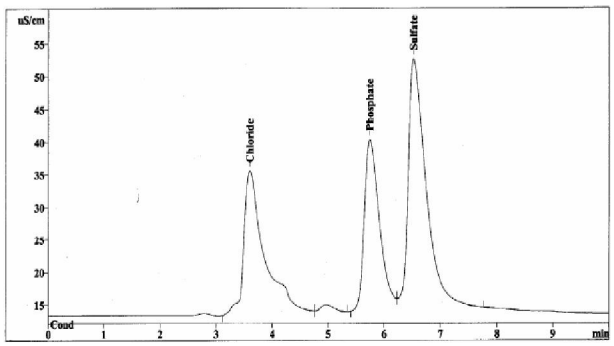


Anions identified in orange juice

Figure 1 : Cations identified in orange juice (ratio/concentration/RT) are sodium (1.88/3.55 mg/L/2.82 min), potassium (119.6/225.5 mg/L/4.28 min), calcium (1/1.89 mg/L/5.64 min), and magnesium (2.2/4.12 mg/L/7.82 min). Anions identified (ratios/concentrations/RT) included phosphate (17.17/67.7 mg/L/5.92 min), sulfate (3.63/14.3 mg/L/6.46 min), and chloride (1/3.94 mg/L/3.57 min)



Cations identified in diet coke

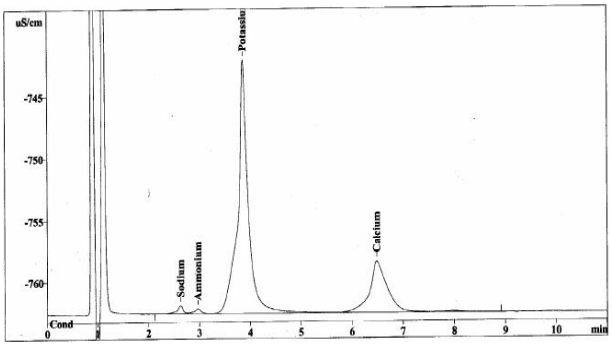


Anions identified in diet coke

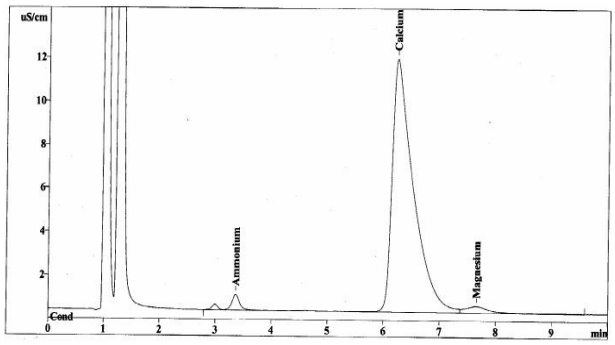
Figure 2 : Cations identified in diet coke included (ratio/concentration/RT) magnesium (1/9.00 mg/L/7.59 min), calcium (5.41/48.7 mg/L/6.35 min), potassium (14.6/131.3 mg/L /4.34 min), ammonium (5.19/46.7 mg/L/3.18 min), and sodium (7.84/ 70.56 mg/L/2.86 min). Anions included chloride (1/74.67 mg/L/3.60 min), phosphate (4.26/318.6 mg/L /5.74 min), and sulfate (2.49/185.6 mg/L/6.52 min)

the amounts of magnesium and ammonium (Figure 3). Chloride and sulfate anions were also identified in small amounts by anion exchange chromatography. Bananas are touted as excellent sources of particular nutritive ions which is corroborated by cation and anion chromatography accomplished following extraction into distilled water. The types of cations identified in order of elution (Figure 4) are sodium, ammonium, potassium, calcium, and magnesium. Their relative abundance ratios by mass per volume are 2.08:1:248.9:14.7:25.2, respectively. Potassium is clearly the dominant ion species which supports the contention that bananas are an effective source for the ions potassium, calcium, and magnesium. Also discerned by anion chromatography in order of elution are chloride, nitrate, and phosphate. The bulk of phosphate in the body is located in the bones and is important in all the organs and tissues of the body with even notable activity in acidifying the urine[14]. Relative ratio of abundance by mass per liter for chloride, nitrate, and phosphate are seen to be 24.4:1:50.8, respectively. Magnesium is the second most plentiful cation within cellular fluids and is an important activator of many enzyme systems found in the body[14]. Bananas appear to supply a multitude of useful mineral species significant to the avowed athlete as well as daily nutritional needs.

Two athletic focused nutritive drinks are Powerade Zero and Gatorade G-2. Following dilution these mixtures were injected into the instruments (Figure 5) revealing that sodium and potassium are common to both. Powerade Zero also contained a significant amount of calcium and magnesium. The anion species chloride, phosphate, and sulfate are common to both mixtures. The ratios of these anion species differed greatly between the two mixtures with that of Gatorade G-2 having chloride, phosphate, sulfate in ratios 11.49:4.44:1

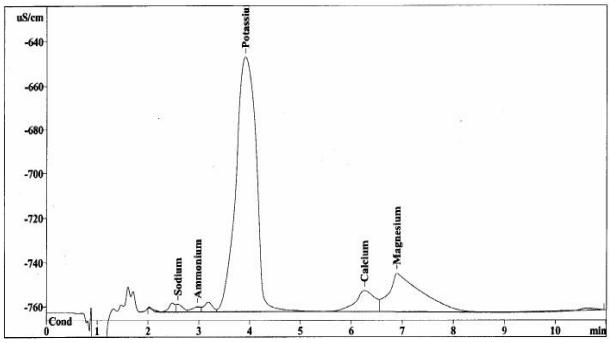


Cations identified in potassium citrate tablet

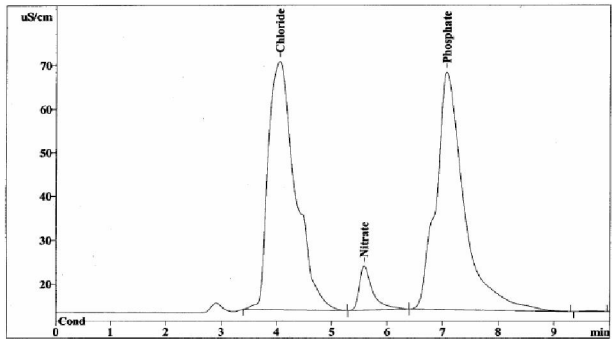


Cations identified in antacid calcium carbonate tablet

Figure 3 : Cations identified in potassium citrate pill (ratio/concentration/RT) include sodium (2.56/0.937 mg/L/2.63 min), ammonium (1:0.365 mg/L/2.97 min), potassium (163.0/59.48 mg/L/3.86 min), and calcium (24.6:8.97 mg/L/6.49 min). For anions (not shown), choride (1/2.95 mg/L/3.56 min) and phosphate (9.5/28.1 mg/L/5.65 min). For antacid tablet, cations included ammonium (1/0.46 mg/L/3.36 min), magnesium (6.53/2.98 mg/L/7.65 min), and calcium (57.1/26.12 mg/L/6.24 min). For antacid tablet anions (not shown), included chloride (1/2.88 mg/L/3.63 min) and sulfate (2.26/6.52 mg/L/6.91 min)

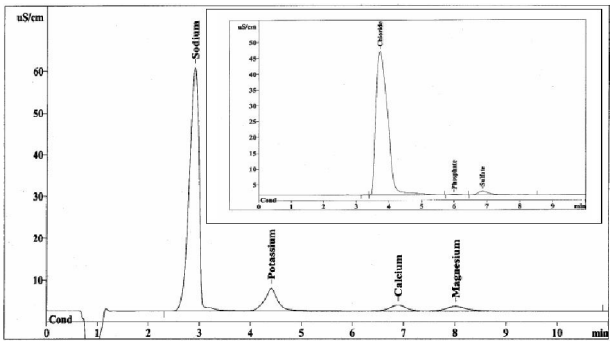


Cations identified in banana

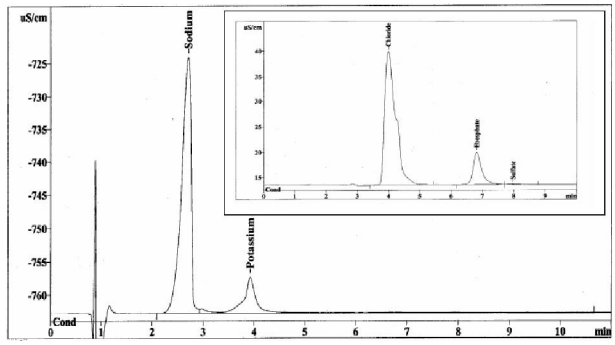


Anions identified in banana

Figure 4 : For uncooked banana the cations (ratio/concentration/RT) included ammonium (1/2.58 mg/L/2.97 min), sodium (2.08/5.36 mg/L/2.59 min), potassium (248.9/641.2 mg/L /3.91 min), calcium (14.7/37.97 mg/L/6.26 min), and magnesium (25.2/64.9 mg/L/6.9 min). For found anions, chloride (24.4/233.9 mg/L/4.05 min), nitrate (1/9.59 mg/L/5.58 min), and phosphate (50.8/483.7 mg/L/7.07 min)



Ions identified in powerade zero



Ions identified in gatorage g-2

Figure 5 : The Powerade Zero cations determined included (ratio/concentration/RT) magnesium (1/1.094 mg/L/8.02 min), calcium (3.77/4.124 mg/L/6.90 min), potassium (19.0/20.08 mg/L/4.41 min), and sodium (77.6/84.88 mg/L/2.91 min). The Powerade Zero anions included, phosphate (1/0.75 mg/L/6.0 min), sulfate (14.5/10.89 mg/L/6.87 min), and chloride (189/141.5 mg/L/3.73 min). For Gatorade G-2 the cations, potassium (1/17.76 mg/L/3.92 min) and sodium (4.69/83.33 mg/L/2.71). For Gatorade G-2 anions, sulfate (1/7.00 mg/L/7.98 min), phosphate (4.44/31.1 mg/L/6.82 min), and chloride (44.5/80.5 mg/L/3.99 min)

and that of Powerade Zero in ratios 188.7:1:14.5, respectively. Chloride represented the dominant anion in both mixtures, but far more in Powerade Zero. Both drinks are used by athletes presumably for support of physiological mineral content.

CONCLUSIONS

Ion chromatography is shown to be a efficacious tool for investigating the ion species available from various over the counter drinks as well as nutrition supplements. The analysis of banana aqueous extract was particularly revealing and corroborates various nutritive assertions made about this fruit. Analysis of the supplements potassium citrate and calcium carbonate confirmed the presence of advertised content as well as the quantity cations with other components. Single column ion chromatography can be utilized to effectively identify ion species in a complex mixture. The parameters and eluents used to conduct both cation exchange and anion exchange chromatography was effective for distinguishing the ion species of interest. Potassium was identified in potassium citrate tablet supplement as well as calcium cation discerned in an over the counter calcium carbonate antacid. Diet coke was injected directly and revealed the presence of five cation species and three significant anion species. Potassium cation was clearly distinguished in an over the counter potassium citrate supplement. Likewise calcium cation was neatly discerned from a distilled water mixture of an antacid tablet ($CaCO_3$). Orange juice was shown to contain a substantial amount of potassium. An extract of banana into distilled water clearly showed the minerals by which banana product are noted for, including sodium, potassium, calcium, magnesium, and ammonium. Whereas anion exchange chromatography identified the species chloride, nitrate, and phosphate. Cation species common to powerade zero and Gatorade G-2 were sodium and potassium. Three anion species common to Powerade Zero and Gatorade G-2 were chloride, phosphate, and sulfate. Therefore ion chromatography revealed nutritive useful information concerning various over the counter supplements and several common food products.

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