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Review

Determination of inorganic ions in food and beverages by capillary electrophoresis

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Abstract

A review of the applications of electrophoresis to the determination of inorganic anions (sulphate, sulphite, phosphate, nitrate, nitrite and halides) and inorganic cations (ammonium, alkali and alkaline metals and trace elements) in food and beverages is presented.

Keywords: Food analysis; Beverages; Reviews; Inorganic anions; Inorganic cations

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1. Introduction

Healthy food is now of concern to most people. In the food industry there is need for the analysis of components in both raw and processed products. All analytical methods are utilized in the development of food products and in controlling food safety. New analytical techniques are being developed and existing techniques optimized. Until recently, high-performance liquid chromatography (HPLC) and gas chromatography (GC) have been the main tools in food analysis. However, with the general exception of lipids, capillary electrophoresis (CE) can be used to examine most food components. This technique is becoming a popular and a viable alternative to ion chromatography for the analysis of inorganic and organic ions in foods, as evidenced by the substantial number of reviews in this area of analysis [1–13]. The relative properties of HPLC and CE are now often discussed [14–16].

Food is a complex inhomogeneous mixture of chemical substances. The isolation and measurement of individual chemical compounds in food represents a difficult task. Procedure for preparation of the sample should be developed and evaluated as an integral part of any analytical method. There are three steps involved in sample preparation of foods: (1) sampling, (2) homogenization, (3) sample preparation. The final step of the analysis is the electrophoresis. Usually the analyst has little influence on sampling. Ideally the analyst should take the samples personally. Literature concerning sampling is generally not easy to locate. The American Chemical Society has published guidelines [17] regarding sampling. International Standards are complete for sampling of fruit and vegetables [18], meat [19], and oilseeds [20]. The complex structure and composition of food necessitates homogenization prior to most electrophoretic analysis. There are two functions of homogenization, reduction of particle size and mixing. The degree of homogenization may affect the accuracy and the precision of the analysis; in ways that may not be revealed by recovery data. Sample preparation includes any operation performed to the test sample prior to injection into the CE; weighing, dilution, clean-up, extraction, digestion, purification, etc. Very little information is available on sample clean-up for CE. Aqueous samples often require very simple sample pretreatment, dilution and/or filtration. These also apply to many beverages, but not to solid food samples. The extraction of ionic species from solid samples prior to CE analysis can often be achieved by heating a mixture of the homogenized sample with water or extractant in a blender or an ultrasonic bath. After dissolving, a further clean-up stage is often essential before injection. Clean-up methods include: filtration, selective removal of the analyte from the sample and elimination of interfering matrix components. Certain types of samples can interact with walls of capillaries. A sample that was found to modify the wall of the capillary was brewed coffee. Increased migration times were observed after every injection of the sample. This migration time shift could be eliminated with an automated three-stage rinse cycle of 100 m*M* lithium hydroxide for 2 min, 18 MΩ water for 1 min and running electrolyte (0.5 m*M* OFM Anion-BT, pH 8.0) for 2 min, performed between sample injections [21]. The deproteination step is often not necessary in the sample extraction procedure in CE determination, because proteins usually migrate much more slowly than small ions, and can therefore be flushed out of the capillary between the runs. The proteins might lead to fouling of the uncoated silica capillary, but with proper rinsing procedures one can avoid this problem. When cations are determined, wet acid digestion is commonly used to dissolve products such as foodstuffs and plants. The acid digestion is often carried out in a closed-vessel system and assisted by microwave heating, which ensure rapid sample preparation with minimized contamination and reduced loss of analytes. While most analytical methods may be affected by sample matrix, the CE techniques are particularly vulnerable. Hence, sample matrix problems constitute one of the biggest limitation of CE methods. In CE, the most commonly encountered sample matrix problems arise when the analyte of interest is present at a relatively much lower concentration than other species measured under the same conditions. The matrix components can mask, broaden, or change the migration time peaks of interest. Several approaches have been suggested to overcome simple problems. Optimizing the electrolyte conditions for a particular analysis by controlling the electrolyte pH, composition and ionic strength have been shown to solve a

limited range of problems. As an example, by increasing the concentration of the electroosmotic flow modifier from 0.5 to 1.5 m*M*, 1 ppm chloride can be separated from 1000 ppm sulphate [21]. Adding organic solvents to the buffer is another way to change the separation selectivity and is found useful for analyzing small amount of iodide in the presence of large excess of sulphate [22]. The use of membrane-based solid-phase extraction (SPE) disks as a sample clean-up technique for anion analysis by CE is discussed [23]. By treating the sample with Novo-Clean IC-Ba, 10 ppm chloride, bromide, nitrate, nitrite, fluoride, and phosphate can be separated from 500 ppm sulphate. A relatively new approach to solving matrix problems is the use of on-line dialysis performed in a flow-injection analysis (FIA) system [24].

A number of CE techniques are in various stages of development at this time. It is very easy to run pure standards in CE but running food samples is much more difficult. The authors wish to point out some needy areas and where some of these techniques are more likely to find applications in future food research. Table 1 categorizes the different applications by type of material analyzed and provides some details on the experimental conditions. Mineral water analysis is not included in the present review as this group is generally included in the environmental one.

2. Inorganic anions

2.1. Sulphur species

2.1.1. Sulphite

Sulphites have long been used as preservatives in foods. There are three functions performed by sulphiting agents (sulphur dioxide, sulphite, hydrogen sulphite and metabisulphite) in food products: antimicrobial agents, antioxidant and browning inhibitor. Sulphite added to food is present in free or bound forms. Bounded sulphite consists of reversibly and irreversibly bound forms. The reversibly bounded sulphite may be released either by an alkaline treatment or more slowly by distillation with acid. Irreversibly bounded sulphites, which form very stable addition compounds, are not detected by most analytical techniques. The sum of free and reversibly bounded sulphite is referred to as total sulphite [25]. In recent years the ingestion of foods containing sulphite implicated the asthmatic reactions and caused several deaths [26]. The US Food and Drug Administration required sulphite declaration on the label of any food containing >10 ppm amounts of sulphite [27].

A lot of analytical procedures have been developed to quantify the sulphiting agents expressed as SO_2 in food. The Monier–Williams method [28,29] is the most common indirect procedure for quantifying sulphite in foods and beverages, traditionally adopted as the official method in many countries. GC, HPLC, FIA and enzyme methods has been reviewed recently [30].

Trenerry [31] described CE method for the determination of sulphite as sulphate in a variety of foods and beverages using a Monier–Williams distillation to liberate sulphur dioxide, subsequent oxidation of sulphur dioxide to sulphuric acid followed by the determination of sulphate by CE. Nitrate was used as the internal standard. The separation of sulphate and nitrate was achieved using 0.5 m*M* OFM Anion-BT, 5 m*M* sodium chromate (pH 8.0) buffer. The CE procedure was first validated with standard solutions to determine the linear range and to check the repeatability of the technique. The detector response for sulphate was shown to be linear to 50 μg/ml and the instrument repeatability data for area calculation (R.S.D.s) were in the range 1.4–8.5%. Limit of detection is 5 mg/kg. The sulphite content of a number of samples (beverages, fresh vegetables, processed foods, seafood) was determined by CE and compared with the levels determined by titrimetry. The levels of sulphite in the products are in good agreement except for one sample of fresh prawns, fresh garlic and some processed foods containing garlic and onion, where the levels determined by CE are lower. This method monitors sulphate levels free from other volatile compounds that might interfere with the acid–base titration.

2.1.2. Sulphate

Sulphate concentration can be affected by the technological use of sulphite. Sulphur and its compounds (e.g., cooper sulphate) find a remarkable use

Table 1
Summary of applications of electrophoresis to food analysis

Carrier electrolyte composition, voltage applied, effective capillary length×I.D., injection, detection	Analyte	Sample matrix	Sample preparation	Validation	Ref.
5 m*M* chromate, 0.4 m*M* OFM Anion-BT, pH 8.0, −30 kV, 52 cm×50 μm, electromigration at 1 kV for 15 s, indirect UV	36 anions	Standards			[21]
5 m*M* chromate, 0.5 m*M* OFM Anion-BT, pH 8.0, −15 kV, 50 cm×75 μm, vacuum level 2, 10 kPa s, indirect UV 254 nm	Sulphite	Cordial, wine, fresh vegetables processed foods and seafood	Distilled, oxidated and filtered	Linear to 50 μg/ml LOD 5 mg/kg, R.S.D. in peak are 1.4–8.5%, compared with titrimetry	[31]
5 m*M* phthalate, 0.5 m*M* OFM Anion-BT, pH 7.0, −20 kV, 100 cm×75 μm, hydrostatic 10 cm for 45 s, indirect UV 254 nm	Bromide, chloride, sulphate, sulphite, nitrate, nitrite, fluoride, phosphate and carbonate	Standards and organic acids in juice	Diluted		[32]
5 m*M* chromate, 0.001% HDB, 20% ANT, pH 11.0, −30 kV, 24.5 cm×50 μm, hydrostatic 10 cm for 10 s, indirect UV 185 nm	Thiosulphate, chloride, sulphate oxalate, sulphite and carbonate	Standards			[33]
10 m*M* chromate, 2.3 m*M* CTAB, pH 11.5, −20 kV (HCLM) or −15 kV (LCLM) 52 cm×75 μm, hydrostatic 10 cm for 10 s, electromigration at 10 kV for 10 s, indirect UV 254 nm	Nitrate and nitrite	Fifteen fresh vegetables	Incubated for 30 min at about 50°C and filtered	HCLM linearity 1–8 μg/ml nitrite, 1–10 μg/ml nitrate, LOQ 1 μg/ml, LCLM linearity 0.1–2.5 μg/ml nitrite 0.1–1.6 μg/ml nitrate, LOQ 0.1 μg/ml, compared with spectophotometry	[35]
5 m*M* chromate, 0.5 m*M* OFM Anion-BT, pH 8.0, negative, 60 cm×75 μm, hydrostatic 10 cm for 30 s, indirect UV 254 nm	Bromide, chloride, sulphate, nitrite, nitrate, fluoride and phosphate	Standards			[43]

Table 1 (*continued*)

Carrier electrolyte composition, voltage applied, effective capillary length×I.D., injection, detection	Analyte	Sample matrix	Sample preparation	Validation	Ref.
5 m*M* phthalate, 0.5 m*M* DTAB, pH 4.2, −20 kV, 45 cm×75 μm, vacuum of 1.5 p.s.i. for 1 s, indirect UV 250 nm	*Ortho*-, pyro- and tripoly-phosphate	Potato baths		Linearity 5–300 μg/ml, R.S.D. in migration time 1.8–3.0% compared with IC	[45]
8.2 m*M* chromate, 0.048 m*M* CTAB, −25 kV 45 cm×50 μm, hydrostatic 10 cm for 20 or 30 s indirect UV 254 nm	Phosphate	Pepsi-Cola mineral and tap water	Diluted	LOD 0.14 ppm	[46]
ITP LE: 8 m*M* HCl 3.5 m*M* β-alanine, 3 m*M* Bis–Tris propane, pH 3.55, 0.1% MHEC, TE: 5 m*M* citric acid, pre-column 16 cm×0.8 mm main column 16 cm×0.3 mm current 200 μA in pre-column and 40 μA in main column, conductivity detection	Nitrate, nitrite, phosphate and sulphate	Ten vegetables	Filtered and diluted	R.S.D. 2.0%	[61]
0.5 m*M* OFM Anion-BT, 1000 ppm chloride, −20 kV, 50 cm×75 μm, vacuum level 2, 20 kPa s, UV 210 nm	Nitrite and nitrate	Cheese, cabbage, fruit juice, water and meat products	Solid samples – blended, filtered, SPE and filtered fruit juice – diluted, SPE and filtered	Linear to 25 μg/ml LOQ 0.2 μg/ml, R.S.D. in peak area 1.2–10.7%	[64]
0.5 m*M* Ce(III) sulphate, 2.5 m*M* 18-crown-6, +30 kV, 55 cm×75 μm, electromigration at 20 (5) kV for 10 s, hydrostatic 10 cm for 30 s, fluorescence, excitation 251 nm, emission 345 nm	Ammonium, potassium, sodium and calcium	Cola beverages		LOD 1–3 μ*M* (hydrostatic), LOD 0.1–0.3 μ*M* (electromigration) linearity 1–1200 μ*M* (hydrostatic)	[93]
5 m*M* UVCat-1, 8 m*M* HIBA, pH 4.4, +20 kV, 52 cm×75 μm, hydrostatic 10 cm for 30 s, indirect UV 185 nm	Potassium, calcium, sodium and magnesium	Orange juice	Diluted 1:100	LOD ppb levels, linear to 100× LOD, R.S.D. in peak area <2% R.S.D. in migration time <0.9%	[96]
5 m*M* UVCat-1, 30 m*M* HIBA, pH 4.4, +20 kV, 60 cm×75 μm, hydrostatic 10 cm for 30 s, indirect UV 214 nm	Potassium, sodium, calcium and magnesium	Multiple electrolyte solutions for parenteral use	Diluted so that the level of sodium is below 80 ppm	Linearity 5–50 ppm, LOQ 5 ppm (Na, Ca, Mg), 20 ppm (K) R.S.D. in peak area 2%	[97]

(*continued on next page*)

Table 1 (*continued*)

Carrier electrolyte composition, voltage applied, effective capillary length×I.D., injection, detection	Analyte	Sample matrix	Sample preparation	Validation	Ref.
CZE 20 m*M* sodium tetraborate, 2.0 m*M* EDTA pH 9.2, +20 kV, 25 cm×50 μm, 12 nl was injected by vacuum for 30 s, UV 200 nm	Calcium	Vegetables	Boiled for 15–20 min and filtered	LOD 0.26 mg/l linear to 25 mg/l, R.S.D. in peak area <3%, R.S.D. in migration time <0.5%, recovery 96–111%	[98]
ITP LE: 5 m*M* HCl, Tris, pH 8.5, 0.1% HPMC, TE: 10 m*M* sodium hexanoate, 0.5 m*M* EDTA, pre-column 15 cm×1.0 mm, main column 15 cm×0.5 cm, current 200 μA for 8 min, then reduced to 50 μA, potential gradient detection	Calcium	Vegetables	Boiled for 15–20 min and filtered	ITP linear 0–25 mg/l	[98]
Ethyleneglycol and EDTA in borate buffer, pH 9.2, −20 kV, 50 cm×75 μm, UV 200 nm	Calcium and magnesium	Wheat flour	Extracted with EDTA	R.S.D. 2–4%, compared with AAS	[99]
5 m*M* UV Cat-1, 6.5 m*M* HIBA, pH 4.4, +20 kV, 60 cm×75 μm, hydrostatic 10 cm for 30 s, indirect UV 214 nm	Potassium, calcium, sodium and magnesium	Milk	Ultrafiltered and diluted 1:250	R.S.D. 5.2% for Na, 6% for Ca, 6.9% for Mg compared with AAS	[101]
Chromate, OFM Anion-BT, −20 kV, 60 cm×75 μm, hydrostatic 10 cm for 30 s, indirect UV 254 nm	Chloride, sulphate, citrate, phosphate, lactate	Milk	Ultrafiltered and diluted 1:250	R.S.D. 2.7% for chloride, 5.7% for citrate, 4.5% for phosphate carbonate and	
Paper electrophoresis, 0.25 M acetate buffer, pH 6.5, potantial of 1000 V applied for 30 min, 2×48 cm strips of Whatman 3-mm filter paper, 50 μl of the sample was injected, NaI (Tl) scintilation	Zinc and selenium	Rice leaves and rice grains	Digested with mixture of HNO_3 and H_2SO_4, adjusted to pH 6.5 with NaOH		[104]
5 m*M* UVCat-1, 6.5 m*M* HIBA, pH 4.2, +20 kV, 60 cm×75 μm, hydrostatic 10 cm for 30 s, indirect UV 214 nm	Potassium, sodium, magnesium, manganese and zinc	Fermentation broth sample	Diluted 1:100	LOD 18–394 ppb, linearity 100× LOD, R.S.D. in peak area <3%, R.S.D. in migration time <1%	[112]

Table 1 (*continued*)

Carrier electrolyte composition, voltage applied, effective capillary length×I.D., injection, detection	Analyte	Sample matrix	Sample preparation	Validation	Ref.
5 m*M* imidazole, H_2SO_4, pH 4.5, +20 kV, 60 cm×75 μm, hydrostatic 10 cm for 30 s, indirect UV 214 nm	Potassium, sodium, calcium and magnesium	Apple juice and orange juice	Diluted 50-fold, filtered	Linearity 05–20 μg/ml (K, Na, Ca), 0.5–10 μg/ml (Mg), 0.5–6 μg/ml (Mn), LOD 100 μg/l (K, Na, Ca, Mn), 50 μg/ml (Mg) R.S.D. <5%, recovery 93–105% compared to FAS	[114]
5 m*M* imidazole, 6.5 m*M* HIBA, 20% (v/v) methanol, 0.55 m*M* 18-crown-6, pH 4.5, +20 kV, 60 cm×75 μm, hydrostatic 10 cm for 20 s, indirect UV 214 nm	Potassium, sodium, calcium magnesium, manganese and zinc	Total diet, oyster tissue, fish tissue, bovine liver, pine needles, citrus leaves and tea	Microwave digested and diluted	Linearity 0.5–10 μg/ml, LOQ <600 μg/l except for K, for which LOQ is 2 mg/l	[115]
10 m*M* sodium acetate, acetic acid, pH 4.5, 5 μg/ml dithizone sulphonate −20 kV, 65 cm×100 μm, hydrostatic 10 cm for 30 s, Vis 480 nm	Methylmercury	Fish and crab meat	Extracted with dithizone sulphonate	LOD 2 μg/kg, recovery 82.5%, S.D. 1.63%	[124]

in agriculture due to their fairly good efficacy as pesticides. These compounds being characterized by very low toxicity.

Sulphate is the anion usually determined as the final product of total oxidation of sulphur compounds, when it is necessary to quantitate the total amount of sulphur species. The electrophoretic determination of sulphite and sulphate can be performed at the same time [32,33]. Sulphate can be simultaneously determined together with other ionogenic species of sulphur such as thiosulphate [21,22,33–36], dithionate [36] and thiocyanate [22,36,37] using CE. Optimization of CZE parameters for sulphur speciation was reported [38].

2.2. Phosphorus species

2.2.1. Phosphate, polyphosphate

Phosphates play two key roles in biology. One of these is as structural elements in certain biological components: the sugar–phosphate backbone of nucleic acids, for example, or the calcium phosphate deposits of bones and teeth. The more interesting role involves the transfer of energy. It appears that phosphate represents a universal currency of energy in living organisms. Phosphorous compounds are present in most foods. Inorganic phosphates are used as fertilizers; phosphate and condensed phosphate compounds are used as food acidulants. Polyphosphates are widely used as additives in meat, fruit juice, cheese, etc. Total phosphorous content is one of the parameters used to define product quality [39].

Instrumental analysis of phosphates is commonly done using ion chromatography (IC) [40,41], isotachophoresis (ITP) [42] and CZE [21,34,37,43–46].

Stover and Keffer [45] present the initial separation of *ortho*-, pyro- and tripolyphosphate using CZE. The separation can be accomplished in 5 min using pH 4.2 phthalate buffer with indirect UV detection. Analysis of phosphate in solutions of sodium acid pyrophosphate used for the treatment of potatoes appeared accurate despite the complex

matrix. To check for interferences from common inorganic anions, sulphate, chloride and nitrate standards were analyzed. All three anions migrated ahead of tripolyphosphate. Organic acids extracted from the potatoes should migrate well behind the phosphate species. CZE results were compared with those obtained by IC. Good agreement is seen between the two techniques.

Rapid separation of mixture of 12 anions in 89 s by CE was reported [46]. This method was applied to the determination of phosphate in a Pepsi-Cola beverage.

2.3. Nitrogen species

2.3.1. Nitrate and nitrite

Nitrate and nitrite are common and natural constituents of many foodstuffs. Relatively high levels can occur in vegetables, which are the main source of nitrate in the human diet [47]. Their accuracy can also be the result of a deliberate addition during food processing. Nitrate and nitrite salts have been used as additives in cured meat for centuries. Nitrates by themselves are not active, but they are reduced to nitrites by microorganisms with nitrate reductase activity. Nitrites may be either technological or natural origin. Examples include cured meat products and cheese, where nitrates or nitrites are added for preservation, and beer, in which nitrates and nitrites come from raw materials. Nitrites are also added to certain cheeses to prevent fermentation by butyric acid bacteria belonging to the species *Clostridium tyrobutyricum* [48]. Nitrite can interfere with the oxygen transport system in the body and may result in methaemoglobinaemia. Infants under three months are thought to be more susceptible than adults [49]. The other major concern is formation of carcinogenic *N*-nitroso compounds. The acceptable daily intake (ADI) recommended by the World Health Organization is 220 mg nitrate for an adult person of about 60 kg. For nitrite recommended ADI is 8 mg [50].

2.3.2. N-Nitroso compounds

When foods are exposed to nitrites, foods with high amine contents can be contaminate by *N*-nitroso compounds. *N*-nitroso compounds in foods can originate from natural bacterial reduction of nitrate, but technological processes involved in the preparation, preservation, or cooling of foods are mainly responsible for this contamination. Nitrosoamines can originate from precursors in human body, e.g., in stomach (at pH <3) from secondary amines and nitrites present in food. *N*-Nitroso compounds exhibit mutagenic, carcinogenic, and teratogenic activities. The possible contamination of food by nitrates and nitrites from paper packing must also be taken into account. The nitrate/nitrite concentration in paper is normally lower than 5 ppm. It has been shown that paper packing material contain nitrosoamines [51].

The determination of nitrate and nitrite has already been performed by several techniques. Spectrophotometric [52,53], ion-selective electrode [54] and chromatographic [41,55–57] techniques have been reported.

Recently, CZE [35,43,44,58–65] can be added to this list.

The determination of nitrate and nitrite together with other anions by CZE was first reported by Romano et al. [43]. Their method is based on indirect detection at 254 nm using the carrier electrolyte 5 m*M* chromate–0.5 m*M* Nice-Pak OFM Anion-BT at pH 8.0.

Nitrates were quantified by ITP in milk [60] and vegetables [61].

Nitrates and nitrites were determined in pickles and processed foods [62] and in five cheese types [63] by CE, which avoid matrix type interference of IC.

A rapid and simple CE method for the determining of nitrite and nitrate in a variety of foods has been developed and validated by recovery data and satisfactory proficiency test results [64]. The samples tested were cheese, cabbage puree, fruit juice, water and variety of meat products. Solid samples were blended for 2 min and then filtered. The filtrate was passed through either an IC-RP cartridge or C_{18} Sep-Pak cartridge. The fruit juice was diluted with water, internal standard was added, and the resulting solution passed through C_{18} Sep-Pak cartridge. All final solutions were filtered through a 0.8-μm cellulose acetate filter disc before analysis. Initial work with iodide and tungstate as internal standard was discontinued in favour of thiocyanate, owing to poor resolution of chloride and iodide, and relatively poor peak shape and inconsistent peak areas for tungstate.

Good recoveries of nitrate and nitrite were achieved with thiocyanate as internal standard.

Nitrate and nitrite (and some other anions) were determined in 15 fresh vegetables by CE [35]. The anions were extracted from the vegetables by mixing and diluting the samples with water at 50°C. The CE method is divided into two parts: a high-concentration-level method, HCLM, (for nitrate determination) and a low-concentration-level method, LCLM, (for nitrite determination). These CE methods were compared with a official AOAC reference method [55] for the determination of nitrates in foodstuffs. The proposed CE methods are linear in described range (Table 1) and have an acceptable precision and accuracy for the determination of nitrates and nitrites in vegetables. The LOD of the high-concentration-level CE method is too high for the determination of nitrite, but for the determination of nitrate it is not problem. The concentration of nitrate in the samples is generally sufficiently high for accurate determination. For nitrite, however, a lower LOD is achieved with low-concentration-level CE method. Owing to nitrite toxicity, it is necessary to detect nitrite below the 0.1 μg/ml. An LOD of less than 50 μg/l is sufficient low for determining dangerous amounts of nitrite considering the acceptable daily intake of nitrite. The major advantage of the CE methods is that they are extremely fast, as a run requires only ca. 5 min, whereas in the spectrophotometric method up to 1 h can be required.

Use of ITP for the determination of anions and cations in the sugar production process was assessed by Kvasnička et al. [65]. ITP methods for the determination of alkali and alkaline earth metals, some inorganic anions (chloride, nitrate, sulphate, sulphite and phosphate) and organic anions (oxalate, citrate, lactate, 2-pyrrolidon-5-carboxylate, volatile fatty acids) are described.

2.3.3. Cyanide

Cyanide is naturally present in some vegetables and in fruit seeds. Because of its extreme toxicity, the development of a sensitive and a selective analytical method is desirable. HPLC and IC using various detection methods have been reported for this purpose [66–68]. The indirect fluorescence detection in CE provides the higher sensitivity for cyanide [69], however, there is actually no literature in food analysis.

2.4. Halides

2.4.1. Bromide, bromate

Narrow tolerance limits makes bromide determination very important to avoid risk to human health. High bromide values in soft drinks can derive from the addition of brominated vegetable oils. Determination of low levels of bromate anions are of interest due to their possible carcinogenic properties [70]. Bromate appears as a possible by-product of the ozonation of bromide-rich water (such as drinking water supplies from open sources located near the sea). Currently, the practical quantitation level for bromate in drinking water set by the US Environmental Protection Agency is 10 mg/l based on ion chromatography [71]. Determination of concentration below 0.5 mg/l was reported [72]. It was demonstrated that the low μg/l level can be attained using IC [73,74] with direct UV detection at 204 nm with subsequent decorrelation of the detector signal [74]. Another application relates to the determination of bromate in bakery products. Bromate is employed as a flour bleaching agent and dough improver. A sensitive method for analyzing bromate, chlorite, chlorate and iodate in water by ion chromatography coupled with ionspray tandem mass spectrometry (MS–MS) [75] has been developed (LOQs were: 1, 0.05, 0.05 and 0.5 μg/l for chlorite, chlorate, bromate and iodate, respectively).

2.4.2. Chloride, chlorite

Chloride is one of the most common inorganic anions in foods. Chloride in the form of NaCl is employed as preservatives in foods. The determination of chloride in foods is essential to confirm with legal regulations and to meeting quality control requirements. Chlorite, bleaching agent used in the manufacture of candy products, has been determined by IC with MS detection.

2.4.3. Fluoride

Water represent the main contribution to intake of fluoride. Animals contain relatively small amounts of fluoride, however, some plants can accumulate fluoride in leaves (for example, the tea leaves contain

about 1.8 g F/kg). A correct daily intake of fluoride is necessary for skeletal bone integrity, but excess consumption causes toxicity (fluorosis).

2.4.4. Iodide

The determination of iodine in foods is important because, although it is an essential micronutrient, high levels of iodine in the diet may lead to thyroid-related problems. Because of the low levels at which it may be present and because losses of the element occur during sample digestion, a reliable determination of iodine in foods is very difficult. Milk and dairy products represent the main contribution, in the iodide form, to the dietary intake of iodine. Another important source of iodine is iodate table salt. Iodine occurring in table salt may be in the iodide form, but also in the iodate form, and it can be determined by chromatographic methods. The use of iodine containing feed supplements and teat dips in the farming industry has resulted in significant increase in the concentration of iodide in milk. Because of its toxicity, excessive intake of iodine is cause for health concern [76]. Since from 25% to more than 90% of the dietary intake of iodine is from milk and dairy products in the form of iodide, a simple and reliable method for the routine determination of iodide in such products is desirable [76].

In the most common analytical conditions, CE allows the simultaneous determination of fluoride, chloride, bromide, iodide and some oxy-halogenated species with indirect UV detection [21,34,37,46,77,78].

Amran et al. [79] studied the usefulness of CE for the resolution of bromide, bromate, iodide, iodate, nitrite, nitrate and selenite anions in standard solution. Employing a 25 m*M* phosphate buffer, pH 2.9 anions separated within 15 min. For iodide and bromide, baseline resolution was achieved only at alkaline pH.

Kenney [32] described the determination of organic and inorganic (chloride, bromide, fluoride, sulphate, sulphite, nitrate, nitrite, phosphate and carbonate) ions. Chloride was also identified in the juice and the soy sauce, but was not quantified. The only clean-up necessary was filtration through 0.45-μm filter when pulp was present in the sample.

Fish enteric chloride, bromide, sulphate, nitrate, oxalate, formate, succinate and maleate ions were monitored by CE [80].

A system designed Capillary Ion Analysis is described [81], wherein the ultra-high efficiency of capillary electrophoresis is combined with optimized resolution using osmotic flow modifier and an indirect UV detection method (benzoate, chromate,and phthalate). Use of the system for quantitation of complex mixture of anions and organic acids in brewed coffee is detailed.

Dedieu et al. [82] used CE to analyze low-molecular-weight ions in musts and wines.

CZE of the minor anions (nitrate, chloride, and sulphate) present in orange juice, orange pulpwash, and processing plant water is reported [83]. Concentration of these anions were also determined by HPLC. Results showed good correlation for chloride and sulphate, however, HPLC was unable to detect nitrate due to interference by other compounds in the orange juice/pulpwash and low concentration of nitrate in these samples. The effect of Ca and carbohydrate concentration on separation and quantitation of these three anions was also investigated. Addition of calcium to the electrolyte caused retention time shifts which improved the separation of the anions from citric acid and carbohydrate addition increased retention time, broadened peak, and reduced peak height for each of the three anions.

On-line dialysis coupled to a capillary electrophoresis system for determination small anions was described [24]. On-line dialysis performed in a flow-injection analysis system has been integrated with CE system via a specially designed interface. A wide range of real samples with complicated matrices (milk, juice, slurry liquors from pulp and paper industry) was successfully analysed for anions without any off-line pretreatment using the fully automatized system.

The separation of chloride, nitrate, sulphate, oxalate, tartrate, malate, succinate, citrate, phosphate, acetate and lactate was performed by CZE using UV detection [84]. This method was applied for the simultaneous determination of organic and inorganic anions in food and beverage samples.

3. Inorganic cations

Food provides human and other animal organisms with all the necessary mineral components, including the primary elements such as H, C, O, N, P, K, Na,

Mg, Ca, S and Cl that are needed in all living forms. It also supplies the trace elements Li, B, F, Si, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, Al, Se, Mo, I, W, and others indispensable to the most important processes responsible for proper functioning of the organism [85].

3.1. Ammonium, alkali and alkaline metal cations

The ammonium ion is an indicator of the food quality and it is considered in this group because the ionic mobilities of alkali, alkaline earth metal and ammonium cations in aqueous electrolyte solution under non-complexing conditions are similar.

Sodium, potassium, calcium and magnesium are essential nutrients whose improper levels can lead to health diseases. Rich source of potassium is milk and vegetables (bean, spinach, etc.) Magnesium is very common in food and it is mostly supplied from vegetables as a part of the chlorophyll molecule.

Considerable amounts of calcium are contained in vegetables although major Ca sources are milk and small fish with edible bone etc. Ca exists in vegetables in the form of free Ca (Ca ion), calcium oxalate and other Ca compounds; it is considered that the oxalate depresses the absorption of Ca and Ca bioavailability [86]. The saline components of milk (5–9.5 g/l) consist of many different species which are present as ions, salts or undissociated complexes [87]. The inorganic species are mainly calcium, potassium, magnesium, sodium, chloride and phosphate. Citrate is the most important of the organic anions. Many compounds, such as chloride, sodium and potassium are completely soluble whereas others, such as Ca, Mg, inorganic phosphorous and citrate, are in equilibrium between the liquid and colloidal phases. They take part in the formation of casein micelles and hence can be considered as part of the proteinic structure of the milk. Studies on the distribution of mineral species between the liquid and colloidal phases have been published [88]. Physico-chemical parameters (ionic strength, pH and temperature) influence the equilibrium of milk [89,90]. The saline equilibrium has a direct impact on the coagulation aptitude and cheese-making from milk. For this reason, it is important to study and to control the concentrations of these ions. The dairy industry needs to know the saline equilibria of milk in order to determine the optimum time for starting the production of cheese. Conventional methods of ion analysis are not convenient, they suffer from many limitations and are materials and/or time consuming. moreover, milks are not standardized in proteins, calcium and fats.

Currently, the analysis of cationic nutrients such as Na, K, Mg and Ca in food is a routine procedure using atomic absorption spectrometry or inductively coupled plasma spectroscopy. In both cases, microwave or hot-plate acid digestion as well as combustion oven ashing are used for sample preparation.

CE allows the simultaneous separation of alkali and alkaline earth metal cations plus ammonium with indirect UV [91,92] and fluorescence [93] detection. ITP also provides a complete resolution of alkali and alkaline metal and ammonium cations in one program [94]. Determination of ammonium, potassium, sodium, calcium and magnesium in mineral water [91] and K, Na, Ca, Mg in mineral water and apple vinegar [95] and orange juice [96] is described.

Simultaneous determination of Na, K, Mg and Ca in parenteral solutions is reported [97]. The results of this work demonstrated that Na, K, Ca and Mg can be quantitated simultaneously as long as the sample can be diluted sufficiently so that the level of Na is below approximately 80 ppm, while the other analyte concentrations remain above 5 ppm (20 ppm for K).

It was shown that cerium (III) sulphate is a useful electrolyte for the determination of ammonium, potassium, calcium, sodium and magnesium in cola beverages using CZE with indirect fluorimetric detection [93]. The complex matrix of the cola beverage does not disturb the determination of ions.

A CZE method was developed for the determination of free calcium (calcium ions) in vegetables [98]. Calcium ions were extracted by boiling crushed vegetables in water for 15–20 min, then filtered through a 0.45-μm membrane filter and determined directly by CZE based on complexation with EDTA. The results agreed with those obtained by ITP. The method was also applied for the determination of calcium ion in vegetables cultivated using fermented blue mussels to examine the usefulness of fermented blue mussels as a fertilizer for vegetables. Chinese vegetables were cultivated using fermented blue mussels; the calcium ion content in the vegetables, determined by CZE method, was considered as an index indicating their usefulness as a fertilizer.

Calcium and magnesium were determined in

wheat flour using CZE [99]. Ions were extracted from flour by vortexing for 5 min in a buffer containing EDTA or ethylene glycol-bis-(β-amino-ethylester)-*N*,*N*,*N*′*N*′-tetraacetic acid (EGTA). Levels of Ca and Mg detected in flour from two samples of wheat, using CZE, were 6.6–7.2 and 14.1–15.6 mg/100 g. Analysis time was <25 min and only 1 μl of the sample was required.

Morawski et al. [100] described the feasibility of combining ion chromatography and capillary electrophoresis to generate data on the cationic nutrient content of foods. The microwave digestion procedure was optimized in order to provide a digest which was compatible with the ion chromatographic process. The samples for this study were intended to represent a wide range of the cations of interest and also a diversity of sample matrices. Pretzels (salted), parsley (dried), bread crumbs, parmesan cheese and peanut butter all present different opportunities for matrix related excipients to potentially interfere with the chromatography. However, the combination of the acid–peroxide microwave digestion and coordination IC produce an interference free chromatogram. Sodium, ammonium, potassium, magnesium and calcium were identified in the samples. CE was also applied to the sample digest. Potassium, calcium, sodium and magnesium were resolved with a different selectivity than the IC separation and with no interferences observed. However, with the UV Cat-2-tropolone electrolyte used for this feasibility evaluation, there is a comigration of potassium and ammonium. With the exception of calcium for IC and potassium for CE, the results compare favourably to AAS. CE offers the advantage of speed with run times of 4.5 min versus 20 min for IC. This speed provides a better compliment to the microwave digestion scheme since a batch of 10-sample scan now be analyzed in a shorter time than is required to digest another batch of 10 samples.

Effect of temperature on the salt balance in milk was studied by ion electrophoresis [101]. Three different methods to obtain the soluble phase of milk were tested: dialysis, ultracentrifugation and ultrafiltration. The authors selected ultrafiltration as it is faster and requires only a centrifuge. The sample had to be diluted 250-fold before analysis. Complete sample preparation requires about 20 min CE results for calcium were confirmed by atomic absorption spectrometry. The correlation between the two techniques was excellent ($r=0.99$). The determination of cations is not affected by anions. Moreover, a complete analysis for cations and anions is achieved with just one injection. Conventional methods of ion analysis do not have this advantage. The electropherograms of milk ultrafiltrates show peaks for potassium, sodium, calcium, and magnesium cations and chloride, sulphate, phosphate and citrate anions. Both were obtained in less than 6 min. It was concluded that the CE is a very convenient technique for establishing the modifications of ionic equilibria in milk under the influence of temperature changes.

It has been demonstrated using a sea water as an example, that the use of a quaternary amino-coated capillary in the separation of alkali and alkaline earth cations can resolve the peak overlap that occurs when one species with a high concentration dominates [102].

3.2. Trace elements

Most trace elements, especially Fe, Zn, Cu, Co, Ni, Mn, V, Mo and W, form characteristic and stable complexes with numerous bioligants such as amino acids, peptides, proteins, nucleic acids, etc. Rich sources of bioelements are water and food, especially meat, liver, fish, corn, wheat, cereals, beans, nuts, oils, table salt, tea, vegetables and fruits. The most abundant microelement in human organism is iron. It perform numerous biological functions. Iron's unique property of appearing in two oxidation states (Fe^{2+} and Fe^{3+}) that are easily interconvertible and its abundance in nature have brought about, in the course of evaluation, a selection of this element in vital processes. The biological functions of other trace elements are associated with enzyme activity. For instance, zinc enters into the composition of over 80 enzymes [103]. Zinc toxicity may occur due to acidification or zinc contamination of some soils. Plant Zn concentrations are a reflection of the available Zn levels in soils. They also indicate the influence of soil environment. Thus, plant tissue analysis can be helpful in diagnosis or confirming Zn deficiency or toxicity [104]. In addition to Fe and Zn, the third important microelement that occurs most abundantly in living organisms is Cu. Copper is characterized by variable oxidation states (Cu^{+},

Cu^{2+}) and therefore participates in numerous biological redox processes [103]. Selenium has attracted extensive analytical study as an essential element which is nevertheless toxic in excess of a rather narrow range of adequacy [105]. The nutrition bioavailability [106], toxicity [107]. and cancer chemopreventive properties [106] of the element are chemical species dependent. Selenium-enriched yeast is often used as a selenium source in nutritional supplements and it has been reported recently that their consumption is associated with statistically significant reduction in cancer mortality and total cancer incidence. Selenium deficiency [108] will cause skeletal and cardiac muscle dysfunction. It is known to protect cell membrane from oxidative damage [109], but selenite and selenate has been suspected to have mutagenic effects [110].

A properly planned diet usually provides the human body with all the trace elements indispensable to it. However, some of these elements, including I, F and Se, appear in the diet in insufficient quantities.

The elements that are absolutely toxic for human and other animals include Hg, Pb, Cd, Ba, Sr, Be, Sb and Cr(VI).

The presence of toxic elements in food is associated with dangerous contamination in the environment, in the air, water and/or soil. The nature of many chemical substances found in food is related to the composition and manufacturing process of their packing. Aluminium is a case of particular interest due to its extensive use in packing. Aluminium concentration in food is normally low, less than 5 mg/kg. Recent toxicological evaluation has shown that aluminium is a factor related to Alzheimer's disease [111]. Tin is also a package residue, a large proportion coming from UV scavengers such as organotin used as heat stabilizer in poly(vinyl chloride) sheets. Another health problem has arisen from chemical impurities in manufactured synthetic food colorants. These impurities result from the use of various catalysts in the manufacturing of dyes, such as cooper, lead, zinc, titanium, selenium and chromium compounds. Some countries have determined allowable quantities for various chemical impurities in colorants.

In the analysis of toxic metals in food, one can use various instrumental methods such as atomic absorption spectrometry, atomic emission spectrometry, UV–Vis and infrared absorption spectrometry, fluorescence and diffraction X-ray analysis. potentiometry with membrane electrodes, d.c. and a.c. polarography, pulse polarography, etc.

There are only a few examples of CE analysis of inorganic cations in food considered before.

Various alkali metals, alkaline earth metals, transition metals and lanthanides were separated by CE and factors affecting the separations were studied [112]. The potential for this technique for analysis of potassium, sodium, magnesium, manganese and zinc in fermentation broth sample was shown. The original sample was diluted 1:100 before analysis. In the diluted sample, potassium and sodium are in the 100–1000 ppm range, while the other three analytes (Mg, Mn and Zn) are in the 10–100 ppb range.

Methods for the quantitative analysis of three cations (calcium, iron and zinc) and the qualitative analysis of several anionic species (chloride, sulphate, nitrate, citrate, fumarate, phosphate, carbonate and acetate) from a prenatal vitamin formulation by two different capillary ion electrophoresis methods are reported [113]. Excellent agreement between CE and flame photometry quantitative results for the cation analysis were obtained. Sample preparation consisted of adding a tablet to 500 ml of water adjusted to pH 2.0 with 6 mol/l nitric acid. The solution was then sonicated for 30 min, followed by a 5-min stirring. Resulting solution was filtered, the filtrate was then diluted 1:50 with water and injected.

An imidazole–H_2SO_4 electrolyte was used to perform capillary ion analysis with indirect UV detection [114]. Baseline separation of K, Na, Ca, Mg and Mn was achieved. Large amounts of Na could be separated efficiently without interference with the other analyte cations. The method was validated for the quantitative analysis of pharmaceutical electrolyte solutions and beverages, and compared with flame atomic spectrometry (FAS) for evaluation. The accuracy and precision of CE with hydrostatic injection are acceptable but that of FAS is better. A wider linear range is obtained in CE than in FAS. The limit of detection for CE is poorer than that for FAS. As in most analytical techniques, matrix effects arise in CE. The CE method is comparatively more susceptible to matrix interferences and a sample pretreatment may be necessary. However. it is possible in CE to detect different

elements simultaneously, but it is not the case in FAS, thus making the new approach very attractive. CE may therefore be a promising technique for process analysis.

Five metal cations (K, Na, Ca, Mg and Mn) were detected in Chinese tea solution [92] using CE. The tea infusion was prepared in the following way: ca. 0.5 g of each of teas was weighed and infused in 15 ml of boiling Milli-Q water for 10 min. The infusions were then filtered through a 0.45-μm syringe filter. For the analysis, the solutions were diluted two-fold or 600-fold.

A CE procedure was developed and validated for the determination of K, Na, Ca, Mg and Mn in food and botanical materials [115]. Closed-vessel microwave acid digestion (HNO_3–H_2O_2, 2:0.5) was used for the sample preparation. Digests of these samples were diluted with water and the resulting solutions injected for CE. The excess of nitric acid in the samples was found to influence the analytical performance, so its effect was investigated in detail. The separation of the five cations becomes worse with increasing nitric acid concentration, and finally is lost when the nitric acid concentration reaches 40 m*M*. However, in the range 0–8 m*M* nitric acid the time-corrected peak areas are constant for Na, Ca and Mg while they show a slight decrease for K and Mn. Therefore, direct determination appears to be possible in the presence of up to about 8 m*M* HNO_3 in the samples. The method of standard addition was used to detect matrix effects. It was performed on the total diet, bovine liver and two tea samples. The standard addition lines were obtained from 50-fold dilution of their digest. The statistical results indicate the absence of important matrix effects.

A method is described which combines [104] radiotracer techniques with paper electrophoresis to investigate the optimal decomposition conditions for zinc and selenium in rice leaf and grain samples. After administration of the respective nuclides of ^{65}Zn and ^{75}Se solutions to the rice, samples of the tested rice are harvested and decomposed with a nitric and sulphuric acid mixture. The completeness of decomposition is investigated by measuring the respective radionuclide-containing species in the decomposed samples by electrophoresis. The results indicate that the Se-containing rice samples are more easily decomposed that those containing zinc. Different decomposition effects are observed between a concentrated nitric–concentrated sulphuric acid mixture (3:1, v/v) and one which includes hydrogen peroxide. The results show that addition of H_2O_2 as an oxidant to the digestion solution of HNO_3–H_2SO_4 can effectively facilitate the decomposition of sample matrices.

Optimization of CZE parameters for selenium speciation were reported by several investigators [116,117]. Simultaneous analysis of inorganic and organic lead, mercury and selenium by CZE with nitrilotriacetic acid as derivatization agent was developed; detection limits down to 0.2 ng/ml were obtained [118].

Clearly progress has been made in speciating mercury by CZE [119–124].

Medina et al. [121] developed a modified two stage Westoo extraction procedure followed by CE for the determination of organomercury species in fish flesh. This technique has been further investigated by Carro-Diaz et al. [122,123]. Hardy and Jones [124] have also been studying CE separation and determination of organomercury species and recently described the CE determination of methylmercury in fish and crab meat after extraction as the dithizone sulphonate complex. The results show that dithizone sulphate can be substituted for cysteine in Westoo procedure and the omission of a third extraction stage made the overall process more efficient and relatively simple. The CE method showed high sensitivity and selectivity, good linearity and excellent day-to-day reproducibility. The low detection limits are sufficient to allow the technique to be applied to wide variety of marine flora and fauna to study methylmercury bioaccumulation in food chains. The lack of substrate and the fact that conditioning the capillary is unnecessary, makes the technique potentially a more useful alternative to GC or LC methods.

4. Conclusions

The analysis of foods and beverages presents a variety of problems which are common to CE and other analytical techniques. These include: a large number of individual components in the mixture, the presence of components that can modify the CE

column and low concentrations of analytes leading to detection difficulties. In CE there has been considerable interest in performing single-step analysis with direct injection of the sample on column. This is quite often feasible in CE because the open capillary columns are less prone to irreversible modification by sample matrix components than a packed chromatographic columns. The advantages of CE method in food analysis are high resolution with short analysis time, low cost of disposables and minimal solvent usage. Because of these characteristics, it has been expected that this technique will soon become an effective complement to current separation method, such as IC, that is now common in the food and beverage analysis.

5. Abbreviations

1 p.s.i.	6894.76 Pa
AAS	Atomic absorption spectrometry
ANT	Acetonitrile
CTAB	Cetyltrimethylammonium bromide
DTAB	Decyltrimethylammonium bromide
EDTA	Ethylenediaminetetraacetic acid
FAS	Flame atomic spectrometry
HDB	Hexadimethrine bromide
HIBA	α-Hydroxyisobutyric acid
HPMC	Hydroxypropylmethylcellulose
LE	Leading electrolyte
LOD	Limit of detection
LOQ	Limit of quantitation
MHEC	Methylhydroxyethylcellulose
R.S.D.	Relative standard deviation
SPE	Solid-phase extraction
TE	Terminating electrolyte
Tris	Tris(hydroxymethyl)aminomethane

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