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Review

State-of-the-art ion chromatographic determination of inorganic ions in food

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Abstract

A review of the applications of ion chromatography (IC) to the determination of inorganic ions in food is presented. The most promising sample preparation techniques, such as accelerated solvent extraction, supercritical fluid extraction, solid-phase extraction, UV photolysis, microwave-oven digestion and pyrohydrolysis are discussed. Among the various inorganic anions, nitrogen, sulphur and phosphorus species and halides are widely determined in foods and to a lesser extent only, cyanide, carbonate, arsenic and selenium species are considered. IC determination of inorganic cations deals with ammonium ion, alkali, alkaline-earth, heavy and transition metals particularly and only a small amount of literature is found on the other ones, like aluminium and platinum. A particular advantage of IC over traditional techniques is the simultaneous determination of several species. © 1997 Elsevier Science B.V.

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

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1. Introduction

Ion chromatography is now a routine technique in food analysis and the number of ion-chromatography (IC) standard methods is growing very rapidly [2–4,42,43,101]. This review deals with the ion chromatographic literature of practical use, related to the determination of inorganic species in foods, thus in many cases we have not referred to the papers that describe the feasibility of ion chromatography in food analysis without taking into consideration real samples.

Tap or mineral water analysis was not included in the present review as these categories are generally included in the environmental ones.

Adequate sample preparation has growing importance because it allows the full exploitation of the potential of ion chromatography, so it is essential to overcome the traditional sample preparation techniques in food analysis, which very often result in solutions that are easily contaminated from the high quantity of reagents involved or prone to causing IC column contamination.

The most widespread detection technique in IC is still conductivity coupled with post-column chemical suppression: this technique has been recently simplified by the introduction of self-regenerating devices [76] that electrolytically hydrolyse water in the eluent stream, in order to produce the ions necessary to the regeneration of the suppressor, thus avoiding the need for a separate regenerant device.

The amperometric detector is also well established in food analysis because of its use in carbohydrate determination, but its applicability has been extended to the inorganic species [27,29,47,108] too. Other detectors have been used in IC determination of inorganic species, with or without post-column derivatization techniques, such as UV-Vis for transition metals determination, inductively coupled plasma (ICP), ICP atomic emission spectrometry (AES), etc.

The anion-exchange columns are been improved in terms of selectivity; speed [87], capacity [31,32] and solvent compatibility. Use of macroporous substrates with chemically grafted ion-exchange sites can reduce the organic anion interference in inorganic anion determination or allow their determination in complex matrices. But improvements in ion-exchange columns were particularly relevant in cation analysis, where the introduction of cation-exchange columns with carboxylic acid based ion-exchange sites [30,48,56,75] allow the separation of alkali and alkaline-earth metals in a few minutes with a simple eluent system. A new column for transition metals determination was introduced that is suitable for use with gradient conditions and, if using temperature control, the analysis can be shortened to less than 10 min [79].

The use of gradient elution in IC for resolving complex matrices is going to be a routine technique [10,28,100] and the interest of food analysts was enhanced by the introduction of a new dedicated

column with higher selectivity and shorter retention times [26,87].

References have been assembled by analyte and are presented in Tables 1–9. Any single row represents a single determination of different species. Species are listed in order of elution. References inside the same table are ordered by date: the last published is the first in the order.

2. Modern sample preparation techniques

In consideration of the few opportunities of injecting food samples directly, or by simple dilution, into the analytical system, the sample preparation plays a vital role in exploiting the potential of ion chromatography. The traditional sample preparation techniques for inorganic species determination in foods generally involve digestion steps like wet digestion, dry ashing or alkaline fusion that require a high quantity of reagents to remove the strong interfering and/or chelating effect of the organic matrix. This kind of sample preparation often results in solutions that are easily contaminated from the reagents involved or prone to causing IC column contamination. In addition conventional sample preparation procedures are time consuming and generate a lot of waste.

Unfortunately it is not possible to use a simple sample treatment technique in food analysis due to the multiplicity of matrix and type and concentration range of the species to be determined.

The modern sample preparation techniques hereby listed are experienced with organic species, and fewer references are reported for inorganic ones. The most promising techniques in order to obtain solutions apt to the direct IC injection seem to be the following:

2.1. Accelerated solvent extraction (ASE)

The accelerated solvent extraction technique employs basically the principles of traditional solvent extraction (whose entire experience can be directly used) but at higher temperature and pressure where solvents show better extraction properties. The high temperature increases the rate of extraction and high pressure elevates the boiling point of the solvent.

This results in better extraction efficiency along with short extraction time and low solvent requirements. The time required for extraction is practically independent of the mass of sample.

The efficiency of extraction is mainly dependent on temperature as it influences physical properties of the sample and its interaction with the liquid phase. The extraction is influenced by the surface tension of the solvent and its penetration into the sample (i.e. its viscosity) and by the diffusion rate and solubility of the analytes: all parameters that are normally improved by the temperature increase. The effect of high pressure is to maintain the liquid phase of solvent beyond its boiling point and also to help penetration of the solvent in the sample matrix. The temperature is normally kept in the range between 50–200°C and the pressure is maintained at 1200–3000 psi.

2.2. Supercritical fluid extraction (SFE)

The supercritical fluid extraction uses the principles of traditional liquid–solid extraction. Supercritical fluids are substances above their critical temperature and pressure and they provide an unusual combination of properties. Supercritical fluids diffuse through solids like gases, but dissolve analytes like liquids, so the extraction rate is enhanced. The most commonly used supercritical fluid is carbon dioxide, which can be used as it is or modified with some percent (1–10%) of an organic solvent.

The solvent strength of any supercritical fluid can be adjusted depending on the pressure and temperature at which the fluid is used (i.e. its density), so allowing a single supercritical fluid to substitute for a variety of conventional solvents.

In supercritical fluid extraction, a pump is used to supply the extraction fluid to the extraction vessel, which is heated to maintain it at a temperature above the critical point. A restrictor device is placed at the end of the system to maintain pressure. During the extraction, the soluble analytes are partitioned from the bulk sample matrix into the supercritical fluid, then swept through the flow restrictor into a collection device.

Supercritical fluid extraction is extensively used for separating organic species from foods (like fats, etc.) and is used for the separation of inorganic

Table 1
Ion chromatographic determination of nitrogen species in foodstuffs

Species	Matrix	Column	Eluent	Detector	Ref.
NO_3^-	Fruits juice	Dionex OmniPac PAX-500	NaOH–ethanol–methanol	Conductivity	[85]
NO_3^-	Beverages, carbonated	Dionex IonPac AS11	NaOH	Conductivity	[28]
NO_3^-	Rice flour Tea leaves	Dionex IonPac AS12A	Na_2CO_3 – NaHCO_3	Conductivity	[14]
NO_3^-	Wine	Shimadzu Shim-pack IC-AI	Phthalic acid	Conductivity	[63]
NO_3^-	Milk	Dionex IonPac AS11	NaOH	Conductivity	[39]
NO_3^-	Carrot juice Vegetables	Metrohm Metrosep Anion Dual 1	Na_2CO_3 – NaHCO_3	Conductivity	[23]
NO_2^-	Orange juice	Hamilton PRP X-100	2,5-Dihydroxy-1,4- benzenedisulphonic acid	UV–Vis	[60]
NO_3^-	Potato chips				
NO_3^-	Pork meat products	Dionex IonPac AS4	$\text{Na}_4\text{B}_2\text{O}_7$	Conductivity	[8]
NO_2^-	Spinach	Dionex IonPac AS4A	Na_2CO_3 – NaHCO_3	Conductivity	[102]
NO_3^-					
NO_3^-	Tea Vegetables	Dionex IonPac AS4	Na_2CO_3 – NaHCO_3	Conductivity/UV–Vis	[12]
NO_2^-	Cereal based baby foods	Waters IC-PAK Anion	KH_2PO_4 – Na_2HPO_4	UV–Vis	[68]
NO_3^-					
NO_2^-	Spinach	Hamilton PRP-X100	Phthalic acid–10% acetone	Coulometry	[11]
NO_2^-	Coffee	Mixed-bed laboratory packed with	Oxalic acid	Conductivity	[25]
NO_3^-	Sake, Japanese Wine	Yokogawa ICS-A23 and Yokogawa CH1			
NO_3^-	Spinach	Dionex IonPac AS4A	Na_2CO_3 – NaHCO_3	Conductivity	[66]
NO_3^-	Beer Wort	Dionex IonPac AS4	Na_2CO_3 – NaHCO_3	Conductivity	[58]
NO_3^-	Wine vinegar	Dionex IonPac AS4A	Na_2CO_3 – NaHCO_3	Conductivity	[33]
NO_2^-	Fruits, syruded canned	Waters IC-PAK Anion	KH_2PO_4 – Na_2HPO_4	UV–Vis	[88]
NO_3^-	Infant foods Jams Marmalades Meats Meats, cured Pork, chopped Vegetables, canned				
NO_2^-	Meats,	Dionex IonPac AS4A	$\text{Na}_4\text{B}_2\text{O}_7$	Conductivity	[34]
NO_3^-	Meats cured				
NO_3^-	Vegetables	Dionex IonPac AS4A	Na_2CO_3 – NaHCO_3	Conductivity	[67]
NO_3^-	Milk Popcorn, buttered Salad dressing	Waters IC-PAK Anion	Sodium octanesulphonate	Conductivity	[51]
NO_3^-	Beer Wort	Dionex OmniPac PAX-500	NaOH–ethanol	Conductivity	[10]
NO_2^-	Food extracts	Alltech Universal Anion	Lithium 4-hydroxybenzoate or Li-hydrogenphthalate or Li-hydrogenphthalate–ethylendiamine	Conductivity	[84]
NO_3^-	Spinach	Dionex IonPac AS4A	Na_2CO_3 – NaHCO_3	Conductivity	[98]

Table 1 (continued)

Species	Matrix	Column	Eluent	Detector	Ref.
NO ₂ ⁻	Meats, cured	Wescan Anion exclusion/HS	H ₂ SO ₄	Amperometry	[54]
NO ₃ ⁻	Vegetables	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[16]
NO ₃ ⁻	Fruits, canned liquor	Dionex IonPac AS5	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[44]
NO ₂ ⁻	Fruits juice	Merck LiChrosorb RP	<i>n</i> -Octylamine–H ₃ PO ₄	UV–Vis	[97]
NO ₃ ⁻	Meats, cured Vegetables				
NO ₃ ⁻	Vegetables	Laboratory packed BAKC Ion exchanger	Potassium gluconate–boric acid or potassium phthalate	Conductivity	[73]
NO ₃ ⁻	Vegetable juice	Waters IC-PAK Anion	Potassium hydrogenphthalate	Conductivity	[20]
NO ₂ ⁻	Beer	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[80]

species too. Unfortunately the selection of supercritical fluids and modifiers is largely empirical because very little analyte solubility data exists for modified supercritical fluids. Interactions between supercritical fluid, target analytes and sorptive sites on the bulk matrix are poorly understood.

2.3. Solid-phase extraction (SPE)

Solid-phase extraction has become very popular over the past ten years. The technique offers many improvements over liquid–liquid extraction and permits both interferent's removal and analytes concentration at the same time.

As the sample solution passes through the sorbent bed, analytes concentrate on its surface, while the other sample components pass through the bed. The most common starting material for sorbent bed is silica, because it is reactive enough to permit its surface to be modified by chemical reaction and yet stable enough to allow its use with a wide range of sample. Polymer based sorbent beds are becoming very popular, thus offering a wide range of selective properties for extraction.

The extraction is performed in four steps: conditioning (the functional groups of the sorbent bed are solvated in order to make them to interact with the samples), retention (the analytes are adsorbed to the bed surface), rinsing (undesired species are removed) and elution (the analytes are desorbed and collected for IC injection).

The extraction conditions are mainly affected by pH, matrix ionic strength, polarity of the elution

solvent, flow-rate and physico-chemical characteristics of the sorbent bed.

2.4. UV photolysis (UVP)

In the preparation of food samples, UV photolysis has shown distinct advantages over traditional dissolution techniques owing to the very low blank values. In Table 10 the reaction mechanisms involved are shown and it is evident that the organic matrix is degraded indirectly via OH radicals and not directly through UV radiation.

It can be seen from the above radical formation reaction that the H₂O quantity is sufficient for producing HO*, however for food samples, where organic matrix is very high, addition of H₂O₂ will accelerate the radical formation resulting into shortening the oxidation time.

Usually high-pressure mercury lamps with a high intensity, as well as a great radiant flux are used. Inserting reflecting surfaces between the sample tubes and the external liquid cooling system to have multiple reflection of UV radiations in the sample enhances the high intensity. An experimental difficulty in the use of these lamps is their high heat development, which can lead to high evaporation losses of the samples, so UV digesters must have cooling systems, which permit oxidation without any losses.

The UV digestion of any sample is directly proportional to the UV intensity and irradiation time. It is inversely proportional to the organic substance concentration. The digestion is also directly proportional to the temperature of the sample; this needs

Table 2
Ion chromatographic determination of sulphur species in foodstuffs

Species	Matrix	Column	Eluent	Detector	Ref.
SO ₄ ²⁻	Tea	Shimadzu Shim-pack IC-AI	Potassium hydrogenphthalate– phthalic acid	Conductivity	[24]
SO ₄ ²⁻	Beverages, carbonated	Dionex IonPac AS11	NaOH	Conductivity	[28]
SO ₃ ²⁻	Beverages Foods	Dionex IonPac ICE-AS1	H ₂ SO ₄	Pulsed amperometry	[27]
SO ₄ ²⁻	Rice flour Tea leaves	Dionex IonPac AS12A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[14]
SO ₄ ²⁻	Wine	Shimadzu Shim-pack IC-AI	Phthalic acid	Conductivity	[63]
SO ₃ ²⁻ SO ₄ ²⁻	Wine, red	Laboratory packed Shiseido Capcell Pak C18, cetyl pyridinium bromide-coated	Phthalate–triethanol- amine–5% methanol	UV–Vis	[61]
SO ₄ ²⁻ S ₂ O ₃ ²⁻ S ₂ O ₆ ²⁻	Orange juice Potato chips	Hamilton PRP X-100	2,5-Dihydroxy-1,4-benzene disulphonic acid	UV–Vis	[60]
SO ₄ ²⁻	Milk	Dionex IonPac AS11	NaOH	Conductivity	[39]
SO ₄ ²⁻	Tea	Shimadzu Shim-pack IC-AI	Phthalic acid–Tris	Conductivity	[35]
SO ₄ ²⁻	Carrot juice Vegetables	Metrohm Metrosep Anion Dual 1	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[23]
SO ₄ ²⁻	Beer	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[13]
S-SO ₄ ²⁻	Liver, bovine	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[70]
SO ₄ ²⁻	Spinach	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[102]
SO ₄ ²⁻	Tea	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[99]
SO ₄ ²⁻	Spinach	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[66]
SO ₄ ²⁻	Beer Wort	Dionex IonPac AS4	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[58]
SO ₄ ²⁻	Wine vinegar	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[33]
SO ₃ ²⁻	Artichokes, canned Fruits juice Mushrooms Sausages Shrimps Tomato sauce Vegetables, canned	Waters IC-PAK Anion	Sodium borate–gluconate	Conductivity	[83]
SO ₄ ²⁻	Tea	Dionex IonPac AS4	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[19]
S-SO ₄ ²⁻	Rapeseed	Waters IC-PAK Anion	Sodium borate–gluconate	Conductivity	[107]
SO ₃ ²⁻	Cola soft drink Corn starch Lemon juice Potatoes, instant mashed Wheat starch Wine	Dionex IonPac AS4A or Dionex IonPac AS2	Na ₂ CO ₃ –NaHCO ₃ –HCOH	Conductivity	[103]

Table 2 (continued)

Species	Matrix	Column	Eluent	Detector	Ref.
SO_4^{2-}	Milk Popcorn, buttered Salad dressing	Waters IC-PAK Anion	Sodium octanesulphonate	Conductivity	[51]
SO_4^{2-}	Beer Wort	Dionex OmniPac PAX-500	NaOH–methanol–ethanol	Conductivity	[10]
SO_4^{2-}	Liver Animal tissues	Dionex IonPac AS4A	Na_2CO_3 – NaHCO_3 –4.5% acetonitrile	Conductivity	[81]
SO_3^{2-}	Cellulosic thixotropic materials	BioRad Aminex HPX-87H ABI Polypore H	H_2SO_4	d.c. Amperometry	[78]
SO_3^{2-}	Beer	Dionex IonPac ICE-AS1	H_2SO_4 –acetonitrile	d.c. Amperometry	[106]
SO_4^{2-}	Food extracts	Alltech Universal Anion	Lithium 4-hydroxybenzoate or lithium–hydrogenphthalate or lithium–hydrogenphthalate– ethylendiamine	Conductivity	[84]
SO_3^{2-}	Beer	Two Dionex IonPac AS2 in series Hamilton PRP-1+ Dionex IonPac AS2	Na_2CO_3 – NaHCO_3 –formaldehyde	Conductivity	[104]
SO_4^{2-}	Milk, human breast	Dionex IonPac AS2	Na_2CO_3 – NaHCO_3	Conductivity	[59]
SO_4^{2-}	Spinach	Dionex IonPac AS4A	Na_2CO_3 – NaHCO_3	Conductivity/ UV–Vis	[98]
SO_3^{2-}	Corn starch Lemon juice Potato, instant mashed Seafood, dehydrated Wine cooler	Wescan Anion exclusion/ HS or Waters or BioRad or Brownlee Polypore H	Sulphuric acid	Amperometry	[53]
SO_3^{2-}	Grapes	Wescan Anion exclusion/ HS	Sulphuric acid	Amperometry	[55]
SO_4^{2-}	Citrus leaves Liver, bovine Tomato leaves	Dionex IonPac AS3	Na_2CO_3 – NaHCO_3	Conductivity	[40]
SO_4^{2-}	Apple Beef Cake Flour Milk, powder Oil	Dionex IonPac AS4A	NaOH– Na_2CO_3	Conductivity	[92]
SO_4^{2-}	Fruits, canned liquor	Dionex IonPac AS5	Na_2CO_3 – NaHCO_3	Conductivity	[44]
SO_4^{2-}	Vegetables juice	Waters IC-PAK Anion	Potassium–hydrogenphthalate	Conductivity	[20]
SO_4^{2-}	Colour additives	Dionex IonPac AS1	Na_2CO_3 – NaHCO_3	Conductivity	[36]

Table 3
Ion chromatographic determination of phosphorus species in foodstuffs (PolyP=Polyphosphates)

Species	Matrix	Column	Eluent	Detector	Ref.
H ₂ PO ₄ ⁻	Tea	Shimadzu Shim-pack IC-AI	Potassium–hydrogenphthalate–phthalic acid	Conductivity	[24]
PolyP	Foods	Dionex IonPac AS11	NaOH	Conductivity	[5]
PO ₄ ³⁻	Cola soft drink	Waters IC-PAK Anion	Sodium gluconate–borate–H ₃ BO ₃ – <i>n</i> -butanol–acetonitrile–glycerol	Conductivity	[6]
PO ₄ ³⁻	Fruits juice	Dionex OmniPac PAX-500	NaOH–ethanol–methanol	Conductivity	[85]
PO ₄ ³⁻	Carrot juice	Metrohm Metrosep Anion	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[23]
	Vegetables	Dual 1			
PO ₄ ³⁻	Cola beverages	Dionex IonPac AS4	Na ₂ CO ₃ –NaOH	Conductivity	[113]
	Soft drinks				
H ₂ PO ₄ ⁻	Orange juice	Hamilton PRP X-100	2,5-Dihydroxy-1,4-benzene-disulphonic acid	UV–Vis	[60]
	Potato chips				
PO ₄ ³⁻	Milk	Dionex IonPac AS11	NaOH	Conductivity	[39]
P-PO ₄ ³⁻	Rice flour	Dionex IonPac AS12A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[14]
	Tea leaves				
PO ₄ ³⁻	Beer	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[13]
H ₂ PO ₄ ⁻	Tea	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[99]
P-PO ₄ ³⁻	Liver, bovine	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[70]
PO ₄ ³⁻	Spinach	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[102]
PO ₄ ³⁻	Vegetables	Waters IC-PAK Anion	Sodium borate–gluconate	Conductivity	[82]
PO ₄ ³⁻	Spinach	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[66]
PO ₄ ³⁻	Beer	Dionex IonPac AS4	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[58]
	Wort				
PolyP	Shrimp, processed	Dionex IonPac AS7	HNO ₃	ICP-AES or UV–Vis	[41]
PO ₄ ³⁻	Wine vinegar	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[33]
HPO ₄ ²⁻	Tea	Dionex IonPac AS4	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[19]
PO ₄ ³⁻	Pea	Laboratory packed with BioRad AG MP-1	Borate–NH ₄ Cl	UV–Vis	[89]
	Tomato, cherry				
PO ₄ ³⁻	Beer	Dionex OmniPac PAX-500	NaOH–ethanol	Conductivity	[10]
	Wort				
PO ₄ ³⁻	Food extracts	Alltech Universal Anion	Lithium 4-hydroxybenzoate	Conductivity	[84]
H ₂ PO ₄ ⁻	Spinach	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[98]
PO ₄ ³⁻	Beer	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[80]
PO ₄ ³⁻	Fruits, canned liquor	Dionex IonPac AS5	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[44]
PO ₄ ³⁻	Flour	Waters IC-PAK Anion	Sodium borate–gluconate	Conductivity	[20]
PO ₄ ³⁻	Potato process water	Waters Resolve C ₁₈	Tetrabutylammonium phosphate–formic acid–methanol	Refractive Index	[20]
PO ₄ ³⁻	Colour additives	Dionex IonPac AS1	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[36]

optimisation keeping in view the volatilisation limits of the analytes.

Appreciable results have been obtained in the trace determination of metals in foods (honey, wine, olive oil, and milk) or plant materials [14].

2.5. Microwave-oven digestion (MOD)

Microwave-oven digestion consists in keeping the

sample and acids in a polytetrafluoroethylene (PTFE) vessel and heating the contents using microwave radiations. The PTFE vessels are transparent to microwaves and the sample directly absorbs electromagnetic energy in MHz–GHz wavelength range which transmits its energy to the polar molecules present in the sample (water, acids, etc.) forcing them to vibrate at high frequency. This results in high sample temperatures without the vessel being heated.

Table 4
Ion chromatographic determination of halides in foodstuffs

Species	Matrix	Column	Eluent	Detector	Ref.
Cl ⁻	Tea	Shimadzu Shim-pack IC-AI	Potassium hydrogenphthalate–phthalic acid	Conductivity	[24]
F ⁻	Beverages	Shimadzu Shim-pack SCR-102H	<i>p</i> -Toluenesulphonic acid	Conductivity	[38]
I ⁻	Food, colouring agents	Carbon BI 01	Tetrabutylammonium hydroxide–Na ₂ CO ₃ –acetonitrile	Conductivity	[71]
Cl ⁻	Wine	Dionex OmniPac PAX-100	NaOH–acetonitrile	Conductivity	[52]
Cl ⁻	Fruits juice	Dionex OmniPac PAX-500	NaOH–ethanol–methanol	Conductivity	[85]
F ⁻	Citrus leaves	Dionex IonPac AS9	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[93]
Br ⁻	Milk, non-fat				
Cl ⁻	powder				
	Orchard leaves				
	Oyster tissue				
	Tomato leaves				
Cl ⁻	Beverages, carbonated	Dionex IonPac AS11	NaOH	Conductivity	[28]
Cl ⁻	Rice flour	Dionex IonPac AS12A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[14]
Br ⁻					
Cl ⁻	Cola beverages	Dionex IonPac AS4+Dionex IonPac AS2	Na ₂ CO ₃ –NaOH	Conductivity	[113]
Cl ⁻	Soft drinks				
Cl ⁻	Wine	Shimadzu Shim-pack IC-AI	Phthalic acid	Conductivity	[63]
F ⁻	Orange juice	Hamilton PRP X-100	2,5-Dihydroxy-1,4-benzene-	UV–Vis	[60]
Cl ⁻	Potato chips		disulphonic acid		
Cl ⁻	Milk	Dionex IonPac AS11	NaOH	Conductivity	[39]
Cl ⁻	Carrot juice	Metrohm Metrosep Anion Dual 1	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[23]
	Vegetables				
I ⁻	Milk products	Dionex IonPac AS11	HNO ₃	d.c. Amperometry	[29]
	Soy-based infant formula				
F ⁻	Coffee	Mixed bed laboratory	Oxalic acid	Conductivity	[25]
Br ⁻	Sake, Japanese	packed with			
Cl ⁻	Wine	Yokogawa ICS-A23 and Yokogawa CHI			
Cl ⁻	Beer	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[13]
Cl ⁻	Liver, bovine	Dionex IonPac AS4A SC	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[70]
F ⁻	Tea	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[99]
Cl ⁻					
Cl ⁻	Spinach	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[66]
	Vegetables				
Br ⁻	Rice	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[105]
F ⁻	Spinach	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[102]
Cl ⁻					
Cl ⁻	Beer	Dionex IonPac AS4	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[58]
	Wort				
Cl ⁻	Wine vinegar	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[33]
Br ⁻	Bakery products	Dionex IonPac AS10	NaOH	ICP-MS	[41]

(Continued on p. 538)

Table 4 (continued)

Species	Matrix	Column	Eluent	Detector	Ref.
Br ⁻	Bread Meats Soups Vegetables Tomato juice	Tosoh TSKgel IC-Anion PWXL	KH ₂ PO ₄ –K ₂ HPO ₄	UV–Vis	[62]
Cl ⁻	Tea	Dionex IonPac AS4	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[19]
Cl ⁻	Milk	Waters IC-PAK Anion	Sodium octanesulphonate	Conductivity	[51]
Br ⁻	Popcorn, buttered				
I ⁻	Salad dressing				
F ⁻	Milk Popcorn, buttered Salad dressing	Waters IC-PAK Ion exclusion	Octanesulphonic acid	Conductivity	[51]
F ⁻	Beer	Dionex OmniPac PAX-500	NaOH–methanol–ethanol	Conductivity	[10]
Br ⁻	Wort				
Cl ⁻					
F ⁻	Food extracts	Alltech Universal Anion	Lithium 4-hydroxybenzoate or lithium hydrogenphthalate or lithium hydrogenphthalate– ethylendiamine	Conductivity	[84]
Br ⁻					
Cl ⁻					
I ⁻	Cod Milk Shell fish Whey powders	Merck LiChrosorb RP	KH ₂ PO ₄ –Na ₂ HPO ₄ – cetyltrimethylammonium bromide	UV–Vis/amperometry	[95]
Cl ⁻	Spinach	Dionex IonPac AS4A	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[98]
F ⁻	Apple Beef Cake Flour Milk, powder Oil	Dionex IonPac AS4A	NaOH–Na ₂ CO ₃	Conductivity	[92]
F ⁻	Fruits, canned	Dionex IonPac AS5	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[44]
Cl ⁻	liquor				
Br ⁻					
Cl ⁻	Agar Cellulose powder Corn starch Gelatin Potato starch Vegetables	Laboratory packed with Dowex AG1	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[69]
Cl ⁻		Laboratory packed BAKC Ion exchanger	Potassium gluconic acid– boric acid or Potassium phthalate	Conductivity	[73]
Cl ⁻	Vegetable juice	Waters IC-PAK Anion	Potassium hydrogenphthalate	Conductivity	[20]
Cl ⁻	Beer	Dionex IonPac AS4	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[80]
Cl ⁻	Certififiable	Dionex IonPac AS1	Na ₂ CO ₃ –NaHCO ₃	Conductivity	[36]
Br ⁻	colours				

Table 5
Ion chromatographic determination of oxyhalides in foodstuffs

Species	Matrix	Column	Eluent	Detector	Ref.
ClO_2^- ClO_3^-	Vegetables rinse water	Dionex IonPac AS12A	Na_2CO_3 – NaHCO_3	Conductivity/ amperometry	[7]
BrO_3^-	Bakery products	Dionex IonPac AS10	NaOH	ICP-MS	[41]
IO_3^-	Milk Popcorn, buttered Salad dressing	Waters IC-PAK Anion	Sodium octanesulphonate	Conductivity	[51]
IO_3^-	Table salt	Merck LiChrosorb RP	NaCl–hexadecyltri- methylammonium chloride	UV–Vis	[95]
IO_3^-	Table salt	Macherey-Nagel Nucleosil 10-NH ₂	NaCl–HCl	UV–Vis	[95]
BrO_3^-	Bread Dough conditioners	Waters IC-PAK Anion	Benzoic acid	Conductivity	[20]
BrO_3^-	Bread	Dionex IonPac AS 1	Sodium tetraborate	Conductivity	[72]

The vessel always remains at a lower temperature than the sample thereby resulting in negligible contamination or absorption of the sample analytes by the vessel.

The digestion is automatically controlled by a pressure and a temperature sensor, at the normal limits of 200°C (at a maximum pressure of 100–150 p.s.i.) and 1200 p.s.i. (at a maximum temperature of 50°C) (1 p.s.i.=6894.76 pa). These limits are imposed by the physical structure of the apparatus and the chemically inert microwave transparent materials used.

Recently an offshoot of MOD has been established using microwaves in conventional solvent extraction technique, known as microwave-assisted solvent extraction (MASE). It may be mentioned here that the molecules with higher dielectric constant absorb more energy from microwaves and attain higher temperatures. The differential temperature between solvent and sample pushes the analyte from sample to the solvent.

Many papers deal with the microwave digestion of food samples [62,64,77]; good results have been obtained in the trace determination of transition metals.

2.6. Pyrohydrolysis (PH)

Pyrohydrolysis is a technique which uses de-

composition of the matrix by superheated water vapours. The apparatus is very simple and consists of a round bottom flask, a quartz delivery tube passing through a small furnace and a condenser; it can be assembled in any analytical chemistry laboratory. The sample is kept in a quartz or platinum or alumina boat inside the delivery tube in the zone of the furnace. Extra pure water is heated and the vapours are pushed using an inert gas through the sample and are condensed. The flowing superheated water vapour extracts volatile and semivolatile substances from the sample, which after condensation are available for analytical determination. The furnace surrounding the sample helps in further heating the water vapours and enhances the volatilisation of analytes.

This technique is normally used for the determination of halogens, borates, nitrates, sulphates, etc. in various food matrices [40,93].

3. Inorganic anions

3.1. Nitrogen species

Nitrite and nitrate: Nitrates are naturally present in many foods, noticeably vegetables where their content varies to a great extent because of the wide-

Table 6
Ion chromatographic determination of other anionic species in foodstuffs

Species	Matrix	Column	Eluent	Detector	Ref.
CrO ₄ ²⁻	Orange juice Potato chips	Hamilton PRP X-100	2,5-Dihydroxy-1,4-benzenedisulphonic acid	UV-Vis	[60]
MnO ₄ ⁻	Orange juice Potato chips	Hamilton PRP X-100	2,5-Dihydroxy-1,4-benzenedisulphonic acid	UV-Vis	[60]
PO ₃ F ²⁻	Orange juice Potato chips	Hamilton PRP X-100	2,5-Dihydroxy-1,4-benzenedisulphonic acid	UV-Vis	[60]
SO ₃ F ⁻	Orange juice Potato chips	Hamilton PRP X-100	2,5-Dihydroxy-1,4-benzenedisulphonic acid	UV-Vis	[60]
SeO ₃ ²⁻ SeO ₄ ²⁻	Orange juice Potato chips	Hamilton PRP X-100	2,5-Dihydroxy-1,4-benzenedisulphonic acid	UV-Vis	[60]
CO ₃ ²⁻	Beverages	Shimadzu Shim-pack SCR 102H	<i>p</i> -Toluenesulphonic acid	Conductivity	[38]
CN ⁻	Flaxseed	Waters IC-PAK Anion	H ₃ BO ₃ -NaOH-Na ₂ CO ₃ - methanol-ethylendiamine	Amperometry	[17]
CN ⁻	Apricot	TSKgel IC-Anion PW	2-Dimethylaminoethanol- formic acid-Na ₄ B ₂ O ₇ - triethylenetetramine-N,N,N',N'',N''',N''''- hexaacetic acid hexasodium salt	Conductivity	[37]
AsO ₃ ⁻ AsO ₄ ³⁻	Liquid health food supplement	Dionex IonPac AS4A	NaOH	ICP-AES	[41]
Total Se	Egg proteins	Laboratory packed with Pharmacia Q-Sepharose Fast Flow	Bis Tris-propane-HCl-NaCl	UV-Vis/FIA-AAS	[46]
Total Se	Milk, goat proteins	Laboratory packed with Pharmacia Q-Sepharose Fast Flow	Imidazole-urea-2-mercaptoethanol-NaCl	UV-Vis/MH-AAS	[21]
PtCl ₆ ²⁻	Bean pod Corn Tobacco	Dionex IonPac AS4A	HCl-NaClO ₄	UV-Vis	[49]
Total Se	Milk, cow proteins	Laboratory packed with Pharmacia Q-Sepharose Fast Flow	Imidazole-urea-2-mercaptoethanol-NaCl	UV-Vis/MH-AAS	[22]
CN ⁻	Chopped fruits	Waters IC-PAK Anion	H ₃ BO ₃ -NaOH-Na ₂ CO ₃ - methanol-ethylendiamine	Amperometry	[18]
HCO ₃ ⁻ CO ₃ ²⁻	Food additives	Dionex ICE-AS1	Octanesulphonic acid	Conductivity	[57]

spread nitrogenous fertilisers' use. Nitrate must be monitored, particularly in infant food preparation, because the reduction in the intestine of nitrate to nitrite can induce methemoglobinemia. In addition, it must be reminded that nitrate, although not very toxic, in the adult digestive tract is reduced under physiological conditions to nitrite, which reacts with secondary and tertiary amines forming high carcinogenic nitrosamines.

Vegetables are not the only source of nitrate intake, the potassium and sodium salts of both nitrate and nitrite are commonly used in food industry, in curing meat for fixing the color, for inhibiting the

microbial growth and for obtaining the characteristic flavour.

The nitrate content is important also for monitoring the food adulteration in dairy industry.

The determination of nitrite and nitrate is usually performed at the same time and mostly by using a bicarbonate/carbonate eluent and suppressed conductivity detection alone or coupled with absorbance in the case of complex matrices.

3.2. Sulphur species

Sulphite, sulphate: Sulphites are commonly used

Table 7

Ion chromatographic determination of I and II group cations and ammonia in foodstuffs

Species	Matrix	Column	Eluent	Detector	Ref.
I group NH_4^+	Beverages, carbonated	Dionex IonPac CS12	Methanesulphonic acid	Conductivity	[28]
II group					
I group NH_4^+	Fruit, juice and puree	Dionex IonPac CS12A	Methanesulphonic acid	Conductivity	[100]
II group					
I group NH_4^+	Ketchup	Laboratory packed with Nomura Chemical Develosil porous silica gel	Benzyltrimethylammonium chloride–acetonitrile	UV–Vis	[65]
Ca^{2+}	Whisky	Hamilton PRP X-100	2,5–Dihydroxy-1,4-benzene- disulphonic acid	UV–Vis	[60]
Mg^{2+}	Orange juice				
I group NH_4^+	Potato chips	Mixed bed laboratory packed with Yokogawa ICS-A23 and Yokogawa CH1	Oxalic acid	Conductivity	[25]
I group	Beverages				
II group	Tea	Dionex IonPac CS3	HCl–2,3-diaminopropionic acid	Conductivity	[99]
I group NH_4^+	Spinach	Dionex IonPac CS1	HCl	Conductivity	[102]
Ca^{2+}	Milk, skimmed	Laboratory packed Dionex PS-DVB 120 Å + Phthalein purple (<i>o</i> -cresolphthalein- 3',3''-bis-methyleneiminodiacetic acid)	KNO_3 –lactic acid	UV–Vis	[50]
Sr^{2+}	powder				
Ba^{2+}					
I group NH_4^+	Bread crumbs	Waters IC-PAK Cation M/D	EDTA– HNO_3	Conductivity	[64]
II group	Cheese				
	Parsley				
	Peanut butter				
	Pretzels				
I group	Tea	Dionex IonPac CS3	HCl–2,3-diaminopropionic acid	Conductivity	[19]
II group NH_4^+	Food simulants	Dionex IonPac CS10	HCl–2,3-diaminopropionic acid	Conductivity	[9]
K^+	Spinach	Dionex IonPac CS1	HCl	Conductivity	[67]
	Vegetables				
I group	Bakery products	Metrohm Super Sep Cation	EDTA	Conductivity	[96]
II group	Cream				
	Diary products				
	Soups, dried				
Na^+	Food extracts	Wescan CATION-R	Lithium hydrogenphthalate or lithium 4-hydroxybenzoate	Conductivity	[84]
K^+					
NH_4^+					
Rb^+					
Mg^{2+}	Food extracts	Wescan CATION-R	Lithium hydrogenphthalate– ethylendiamine	Conductivity	[84]
Ca^{2+}					
Ba^{2+}					
I group N– NH_4^+	Grain	Waters IC-PAK Cation	HNO_3	Conductivity	[45]
Na^+	Grain	Protein Pak SP-5PW	HNO_3 –acetone	Conductivity	[45]
K^+					
N– NH_4^+					
I group NH_4^+	Foods	Metrohm Supersep 125 IC-Cation	Citric acid–pyridine-2,6- dicarboxylic acid	Conductivity	[109]
II group					
I group	Wine	Biotronik BT IV KA	HNO_3	Conductivity	[91]
I group	Wine	Dionex IonPac CS1	HCl	Conductivity	[91]
I group NH_4^+	Molasses	Dionex IonPac CS3	HCl–2,3-diaminopropionic acid	Conductivity	[86]
II group					

(Continued on p. 542)

Table 7 (continued)

Species	Matrix	Column	Eluent	Detector	Ref.
Mg ²⁺ Ca ²⁺	Fruit juice	Macherey-Nagel Nucleosil 5SA	Oxalic acid–ethylenediamine– acetone	Conductivity	[90]
K ⁺	Beer Fruit juice Milk Vegetable juice Wine	Dionex IonPac CS1	HCl	Conductivity	[97]
I group NH ₄ ⁺	Cheese	Waters IC-PAK Cation	HNO ₃	Conductivity	[20]
Mg ²⁺ Ca ²⁺	Wort	Waters IC-PAK Cation	Citric acid–ethylenediamine	Conductivity	[20]
II group	Porridge oats Wine, red	Macherey-Nagel Nucleosil SA10	Tartaric acid	UV–Vis	[110]
I group NH ₄ ⁺	Beer	Dionex IonPac CS1	HCl	Conductivity	[80]
II group	Beer	Dionex IonPac CS1	HCl– <i>m</i> -phenylenediamine	Conductivity	[80]

in the food industry as a preserving agent; only recently has there been focus on the health problems associated with their widespread use. Moreover, the sulphite content is controlled by national and international regulations where sulphite data must be provided for each component of food formulation.

Most of the IC papers concerning sulphur compounds analysis are related to the sulphite determination as previously reviewed [74]; a major improvement was the introduction of pulsed amperometric detection. Sulphate concentration can be affected by the technological use of sulphites. In consideration of the presence of sulphur bound to organic molecules too, sulphate is the anion usually determined as final product of total oxidation of sulphur compounds, when it is necessary to quantitate the total amount of sulphur species. The determination of sulphite if stabilised in a suitable way and sulphate can be performed at the same time.

Sulphate can be simultaneously determined together with other inorganic species of sulphur such as thiosulphate and dithionate.

3.3. Phosphorus species

Phosphate, polyphosphate: Phosphorus compounds are present in most vegetable and animal foods; some of them, such as proteins and phospholipids, are important indicators of metabolic activity. Phosphorus is important for skeletal integrity, that direct-

ly depends on calcium/magnesium/phosphorus ratio. A phosphorus excess leads to tissue ossification.

Inorganic phosphates are extensively used as fertilisers so the same considerations that apply for nitrogen species are also valid for phosphorus content in vegetables. Phosphate determination in foods is very important: for example its concentration in milk affects almost all aspects of cheese manufacturing, in soft drinks formulation where it acts as acidifier and flavour, etc.

Polyphosphates are widely used as additives: in meat-based products for reducing water loss during the commercial life of the food, but they can be also used to increase the uptake of water for economic fraud; in fruit juices as flavour and color preservatives; in the dairy industry as additive for cheese, etc.

Total phosphorus content is one of the parameters used to define product quality and genuineness. The most common way of determining phosphate is its separation with bicarbonate/carbonate eluent followed by suppressed conductivity detection. The gradient IC introduction caused polyphosphate analysis to move from traditional absorbance detection following a post-column reagent addition step to suppressed conductivity.

3.4. Halides

In the most common analytical conditions, ion

Table 8
Ion chromatographic determination of transition and heavy metals in foodstuffs

Species	Matrix	Column	Eluent	Detector	Ref.
Pb ²⁺	Rice flour	Dionex IonPac CS10	H ₂ SO ₄ –HCl–KCl	UV–Vis	[14]
Cd ²⁺	Tea leaves				
Fe ³⁺	Rice flour	Dionex IonPac CS5	Pyridine-2,6-dicarboxylic acid	UV–Vis	[14]
Cu ²⁺	Tea leaves		CH ₃ COOH–CH ₃ COONa		
Ni ²⁺					
Zn ²⁺					
Co ²⁺					
Cu ²⁺	Soybean,	Macherey-Nagel Nucleogel	Tris(hydroxymethyl)amino	ICP-OES	[94]
Zn ²⁺	defatted flour	Pharmacia Superdex	methane–HCl		
Mn ²⁺					
Cd ²⁺	Orange juices	Hamilton PRP X-100	2,5-Dihydroxy-1,4-benzenedisulphonic acid–EDTA	UV–Vis	[60]
Pb ²⁺	Potato chips				
Ni ²⁺					
Cu ²⁺					
Co ²⁺					
Fe ³⁺					
Cr ³⁺					
Cd ²⁺	Oyster tissue	Shimadzu Shim-pack IC–Cl	Lactic acid	UV–Vis	[112]
Pb ²⁺	Wine	Dionex IonPac CS5	Oxalic acid	UV–Vis	[15]
Mn ²⁺	Foods	Metrohm Supersep 125 IC–Cation	Citric acid–pyridine-2,6-dicarboxylic acid	Conductivity	[109]
Zn ²⁺	Wort	Waters IC-PAK Cation	Citric acid–ethylendiamine	Conductivity	[20]
Fe ³⁺	Apples	Dionex IonPac CS2	Sodium sulphosalicylate–ethylenediamine	UV–Vis	[111]
Fe ²⁺	Lentils				
Fe ³⁺	Porridge oats	Macherey-Nagel Nucleosil SA10	Tartaric acid	UV–Vis	[110]
Cu ²⁺	Wine, red				
Pb ²⁺					
Zn ²⁺					
Ni ²⁺					
Co ²⁺					
Cd ²⁺					
Fe ²⁺					
Mn ²⁺					
Fe ³⁺	Porridge oats	Dionex IonPac CS2	Tartaric acid	UV–Vis	[110]
Cu ²⁺	Wine, red				
Ni ²⁺					
Zn ²⁺					
Co ²⁺					
Pb ²⁺					
Fe ²⁺					

Table 9
Ion chromatographic determination of other metals in foodstuffs

Species	Matrix	Column	Eluent	Detector	Ref.
Al ³⁺	Orange juice	Hamilton PRP X-100	2,5-Dihydroxy-1,4-benzenedisulphonic acid–EDTA	UV–Vis	[60]
	Potato chips				
Al ³⁺	Apples	Dionex IonPac CS2	Sodium sulphosalicylate–ethylenediamine	UV–Vis	[111]
Fe ²⁺	Lentils				

Table 10

Reaction mechanisms involved in UV photolysis

● Radical formation:	$\text{H}_2\text{O} + h\nu \rightarrow \text{H}^* + \text{HO}^*$ $\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{HO}^*$
● H_2O_2 decomposition:	$\text{HO}^* + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^*$ $\text{HO}_2^* + \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + \text{H}_2\text{O} + \text{HO}^*$
● Termination reactions:	$\text{HO}^* + \text{e}^- \rightarrow \text{OH}^-$ $\text{HO}^* + \text{H}^* \rightarrow \text{H}_2\text{O}$ $2 \text{HO}^* \rightarrow \text{H}_2\text{O}_2$
● Oxidation reactions:	$\text{HO}^* + \text{CH}_3\text{-CH}_2\text{-OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{-C}^*\text{H-OH}$ $\text{HO}^* + \text{CH}_3\text{-C}^*\text{H-OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{-CHO}$

chromatography allows the simultaneous determination of fluoride, chloride and bromide with suppressed conductivity detection, while iodide is usually determined separately with amperometric detection. For some oxy-halogenated species a good alternative is absorbance detection.

3.4.1. Fluoride

Fluoride is an important factor for skeletal bone integrity and dental health. A correct daily intake is necessary, but excess consumption causes symptoms of acute and chronic fluoride toxicity (fluorosis). The principal source of fluoride intake is water, nevertheless other foods, such as tea and fish can be a source of fluoride. High values of fluoride in milk from cows indicate environmental pollution. In dairy products, such as cream and cheese, fluoride content increases and reaches about three folds the original milk concentration. A relevant quantity of fluoride in meat may be caused by the presence of finely ground osseous material.

3.4.2. Chloride

Chloride is one of the most common inorganic anions in foods. Its content is usually related to the sodium presence and it is very important for metabolic acid–base equilibrium. In the food industry it is commonly added in the form of NaCl as a preserving agent or to enhance the sapidity of the product. Chloride concentrations can vary over a wide range, and its determination is helpful in the definition of the quality. Excess in chloride content creates a series of adverse effects not only on human health but also on technological process steps such as production and storage.

3.4.3. Bromide

The bromide content in foods is related to disinfecting with methyl bromide, some plants such as carrot, tomato, celery and melon accumulate bromide, and its determination can be used as a marker of methyl bromide treatment.

High bromide values in soft drinks can derive from the addition of brominated vegetable oils.

The narrow tolerance limits make the bromide determination very important to avoid risk for human health.

3.4.4. Iodide

Trace iodide is necessary for normal physical and mental development. Common sources of iodide include iodised table salt and seafood, but also other foods, such as eggs and milk, contain iodide. Iodophors used as disinfectants are a possible external source of iodide in dairy products. An incorrect dietary balance can lead to thyroid disorders.

These considerations have led to a concern over both high and low iodide levels in diet and a nutritional labelling requirement for iodide/iodine content.

3.4.5. Oxyhalides

Bromate is a potential carcinogenic agent thus its determination is important at low levels. There is some concern about the health effects on residual bromate in bakery products, because bromate salts are used as dough conditioners in the baking industry. The majority of bromate is reduced to bromide during the baking process; however residual bromate has been found in some baked goods.

Iodate is added to table salt as integrator of iodine

in the diet. Its importance has been previously pointed out under the iodide paragraph.

3.5. Other species

3.5.1. Cyanide

Cyanide is a very toxic compound, concentrations as low as few ppms are dangerous for human health. Cyanide is naturally present in some vegetables, such as cassava, sorghum and in fruit seeds. Its presence in fruit is also related to ethylene biosynthesis, i.e. post-harvesting storage and ripening degree. Cyanide is closely associated with membrane structure and can be released by technological processes involving fruit seed presence. The amperometric detection provides the higher sensitivity for cyanide, even if there is actually no literature in food analysis.

3.5.2. Carbonate

Carbonate is naturally present in fermented beverages or added to the soft drinks. It is usually determined when it is important to evaluate its buffering capacity. In consideration of its weak acidity the separation technique of choice is ion exclusion coupled with conductivity detection.

3.5.3. Arsenic species

Arsenic species are toxic compounds and their presence must be detected at very low levels. The indiscriminate use of arsenical compounds in agriculture at the beginning of this century caused an actual pollution of soil that became an important source of arsenic in foods. Other main sources of arsenic contamination are industrial pollution and the use of water with high arsenic content during the food preparation process.

The use of ion chromatography for arsenic determination provides important toxicity information as various species have widely different toxic effects. In the case of a sophisticated detection technique, such as ICP-AES, not being available, a good way of detecting both arsenite and arsenate is the use of amperometric detection coupled with suppressed conductivity.

3.5.4. Selenium species

Selenium is a fundamental micro-element in nutrition and its deficiency in diet can lead to typical

diseases, such as Keshan disease. Normally selenium is present in trace amounts in proteins, as it substitutes sulphur in aminoacids.

Intensive studies have been done about different concentrations of selenium in foods. An important source of selenium species can also be the waters used during the food processing.

The use of ion chromatography for selenium determination provides important information about oxidation states, because selenite and selenate can be determined in the same analysis.

4. Inorganic cations

Inorganic cations are naturally present in foods and their concentrations can vary in a wide range. Industrial food production processes and modifications occurring during the commercial life of the product or metabolic modifications can change the normal content of different cations.

Ion chromatography allows the simultaneous determination of I and II group cations plus ammonium ion with conductivity detection, while heavy and transition metals are more commonly determined by post-column derivatization technique followed by absorbance detection.

4.1. I and II group cations and ammonium

Group I and II metals are mainly monitored for mass balance purposes. Most of them are essential nutrients whose improper levels can lead to health diseases, so sodium and potassium contents are important for nutritional labelling.

Ammonium ion is an indicator of the food quality and it is considered in this group because of its chromatographic behaviour, in fact it normally elutes in the same chromatographic conditions used for I group cations elution.

Magnesium is very common in food and it is mostly supplied from vegetables as a part of the chlorophyll molecule. There is a strict correlation among magnesium, calcium and phosphorus related to skeletal bone integrity that enhances the importance of the magnesium determination.

Calcium is widespread in food, mostly in complexed form; thus its concentration as ion determin-

able by ion chromatography is often related to the technological process to which the food and/or sample preparation undergoes.

4.2. Heavy and transition metals

During the last decades, evidence has grown on essentially, bioavailability, mobility, retention, accumulation and toxicity of heavy and transition metals in foods.

Normally they are present at trace levels in complex matrices, thus requiring high sensitivity and specificity of the analytical technique chosen. The importance of speciation between ionic forms, such as Cr (VI)/Cr (III) or Fe (III)/Fe (II), due to health concerns associated to some of them, increased the use of ion chromatographic analysis.

4.3. Other metals

There are only a few examples of ion chromatographic analysis of ionic species not considered before.

4.3.1. Aluminium

The use of aluminium and its derivatives, for example in food packaging and agriculture, made its determination at low levels more important, because of its toxicity.

Aluminium is determined by cation-exchange followed by a post-column derivatization technique and absorbance detection.

4.3.2. Platinum

The wide use of catalysts for the purification of car exhaust gases and the increase of its concentration in the environment caused its growing importance. The only example, included in Table 6, is related to its determination as a chloro-complex by anion-exchange separation and absorbance detection.

5. Conclusions

New developments in ion-exchange columns with gradient capabilities, higher capacities coupled with high efficiency, different selectivity, solvent compatibility and major diffusion of ion chromatographic

detection techniques other than conductivity require an update of the most recent and comprehensive review on the subject [74]. Furthermore the recent interest about a promising analytical technique for ionic substances determination, such as capillary zone electrophoresis (CZE), has reduced the attention devoted to an 'established' technique like ion chromatography.

Ion chromatography reliability and versatility was revealed as the winning card in analysing complex matrix typical of food samples, with high selectivity, sensitivity and reproducibility; by now CZE has been not able to establish itself in food analysis [1], where its cumbersome analysis set-up and erratic behaviour complicate the intrinsic instrumental simplicity.

This review also gives evidence that the increased characterisation requirements of components, contaminants or additives, generates the need of ion chromatographic methods for the determination of certain less common ions in food samples. Testing for the possibility of analysing them is actually in progress.

The state-of-the-art ion chromatography will refocus the attention of food chemists on their analytical requirements, because nowadays ion chromatography cannot be merely considered the chloride, nitrate, and sulphate determination technique.

The completion of the present review with the state-of-the-art ion chromatographic determination of organic ions in food will follow in a short time.

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