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Determination of cations in fruit juices and purées by ion chromatography

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Abstract

An isocratic ion chromatographic (IC) method for the separation and determination of the main cations in fruit purées was evaluated. Ion chromatographic separation of Group I and II cations have already been tested with many other matrices; it allowed the simultaneous separation of Na, Ca, Mg, K and ammonium ions by using a new cation-exchange column (Ionpac CS12A), an electrically regenerated suppressor and a conductivity detector. The aim of this work was to evaluate the proposed IC method for fruit products which are characterized by considerable quantitative imbalances among the cations. During the 1994 season several samples of Italian fruit juices and purées were collected and Na, Ca, Mg and K were determined by both atomic absorption spectrometry and IC. The data obtained by IC were suitable for the use in quality and process control in the fruit juices industry.

Keywords: Fruit juice; Food analysis; Inorganic cations

1. Introduction

The determination of cations is one of the most important analyses for the routine quality control of fruit juices and purées [1,2]. Among Group I and II cations, those most relevant in concentration in fruit juices are potassium, magnesium, calcium and sodium. Their content is non only related to the fruit type, but also there are correlations with cultivar, the nature of the soil and fertilization procedures [3,4]. In addition to raw material factors, production technology may have an affect on the cation content; an example is the importance of the quality of water used for nectars and reconstituted juices. In the case of citrus fruit juices, the calcium content depends on the extraction technology and is higher in high-pulp juices [5].

The official method for the determination of cations suggested by the International Federation of Fruit Juices Producers (IFFJU) uses atomic absorption spectrometry (AAS) [6]. Nevertheless, it may be advantageous to have an alternative method for rapid control in less well equipped laboratories.

Ion chromatography (IC) is particularly suitable for this purpose because of its versatility, as the same technique can often be used for the determination of other parameters in food laboratories such as anions and organic acids, etc.; its attributes include speed, as many parameters can be determined in one run, wide availability in laboratories, high precision [7–9] and low maintenance costs.

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Following these considerations, an IC method for the determination of cations, already in use for other matrices, such as wet depositions, surface and tap water and waste water [10–14], was evaluated for fruit juice analysis. Isocratic IC allows the simultaneous determination of Group I and II cations, and isocratic elution is also satisfactory in the case of complex samples such as fruit juices and purées where the imbalance between high contents of some cations (the K concentration ranges up to 3000 mg/kg) and low contents of other cations (the Na concentration can be as low as 10 mg/kg) could complicate the simultaneous analysis.

The method was applied to the analysis of 1994 and 1995 Italian production of purée samples of apricot, pear, peach and blood-orange juices. Cation concentrations were determined by IC and then compared with the results of AAS determination.

2. Experimental

2.1. Reagents and standard solutions

Methanesulfonic acid (purity 99%) was purchased from Aldrich (Gillingham, UK) and used to prepare the eluent at a concentration 20 m*M*.

Working standard solutions were prepared daily by diluting Carlo Erba (Milan, Italy) Normex atomic absorption standards (1.000 g/l) or by dissolving the required Carlo Erba analytical-reagent grade reagents.

2.2. Ion chromatography

The chromatographic system consisted of a Model 305 pump with a titanium head, a Model 805 pump pulsation electronic damper, a Model 231 automated sample injector, equipped with a 25-μl injection loop (Gilson Medical Electronics, Villiers-le-Bel, France) and a Model 431 conductivity detector (Waters, Milford, MA, USA) with 10 μS full-scale, an IonPac CG12A guard column, coupled to an IonPac CS12A analytical column (Dionex, Sunnyvale CA, USA) and a CSRS-II cation self-regenerating suppressor (Dionex) used in the autosuppression recycle mode.

Table 1
Ion chromatographic conditions for Na, K, Mg and Ca

Column	IonPac CG12A + CS12A
Eluent	20 m*M* methanesulfonic acid
Flow-rate	1.0 ml/min
Injection volume	25 μl
Detection	Suppressed conductivity
Suppressor	CSRS-II recycle mode
Controller	Position 2 (100 mA)

Acquisition and integration of chromatograms were performed with an AT 386 personal computer linked with a Gilson Gsioc 506 C system interface.

An analytical water purification system (Smeg, Parma, Italy) was used to produce deionized water of ultrapure quality (18.2 MΩ).

The analytical conditions are summarized in Table 1.

2.3. Sample preparation

Preliminary tests were carried out by comparing simple dilution with water with acidic digestion with HCl in order to improve the dissolution of Group II cations, which could be bound to pectic substances. In this case 1 ml of 5 *M* HCl was added to 5 g of juice or purée of sample, heated for 20 min on a steam-bath, then cooled and made up to 250 ml with DI water.

In the case of the acid-digested samples, there was no improvement in the determination of divalent cations with respect with a simple dilution with water, and an average 15% depression of all peak responses was observed, due to the influence of H^+ on the carboxylic exchange sites. Hence simple dilution with water was chosen for sample preparation, 1:50 or 1:100 (w/v), in order to obtain cation concentrations falling within the linear range of the calibration graphs. The diluted samples were filtered through a 0.45-μm filter before injection.

2.4. Atomic absorption spectrometry

The determinations of Na, K, Mg and Ca were

Table 2
Atomic absorption spectrometric conditions

Element	λ (nm)	Fuel/support	Matrix modifier	Optimum working range (mg/kg)
Na	213.9	Acetylene/air	CsCl	0.1–1
K	228.8	Acetylene/air	CsCl	0.5–2
Mg	232.0	Acetylene/nitrous oxide	$LaCl_3$	0.5–2
Ca	242.5	Acetylene/nitrous oxide	$LaCl_3$	0.5–2

carried out using a Varian (Mulgrave, Victoria, Australia) Model 250 Plus instrument. The sample was diluted before analysis.

In order to avoid chemical interferences, $LaCl_3$ and CsCl matrix modifiers were used both in standards and in samples. The standard concentration, as reported in Table 2 together with other AAS conditions, must fall in a narrow range (Na 0.1–1 mg/l, K 0.5–3 mg/l, Mg 0.5–2 mg/l and Ca 0.5–2 mg/l) in order to obtain the optimum response.

The results were obtained by computerized graphical evaluation by the external standard method, taking into account the matrix modifier dilution.

3. Results and discussion

A preliminary comparison was made between IonPac CS12 and IonPac CS12A cation-exchange columns in order to establish the optimum selectivity. The IonPac CS12A column has phosphonic exchange sites added to the carboxylic exchange sites present in the IonPac CS12 column. The resulting selectivity is better for our purposes, particularly towards sodium and ammonium separation and for the best quantification of sodium in the samples. It also appears to be more robust than the IonPac CS12 towards contamination by polyphenolic substances.

Fig. 1 shows the comparison between the selectivity with the IonPac CS12 and CS12A columns. Fig. 2 shows the typical chromatographic behaviour of the latter in the analysis of different fruit juices and purées.

The possible influence of the sample matrix on the determination of cations was verified by the standard additions method; the calibration graphs were linear ($r > 0.98$) over three order of magnitude of concentration for all the cations considered, giving good coincidence with the calibration graph for a standard. These data and the recoveries which were better than 97% for all the cations considered, demonstrate the negligible influence of the matrix on the cation responses.

Statistical analysis was used to determine the correlation between IC and AAS; the regression coefficients were better than 0.85 and up to 0.95 in the case of potassium. Regression coefficients are reported in Table 3.

A more accurate description of the comparison between AAS and IC is shown in Figs. 3–6

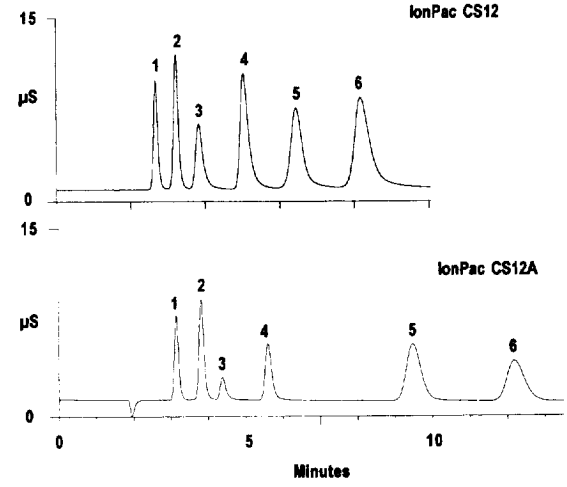

Fig. 1. Comparison between the selectivities of the IonPac CS12 and CS12A columns. Conditions as in Table 1. Peaks: 1 = Li^+ (1 mg/l); 2 = Na^+ (4 mg/l); 3 = NH_4^+ (5 mg/l); 4 = K^+ (1 mg/l); 5 = Mg^{2+} (5 mg/l); 6 = Ca^{2+} (10 mg/l).

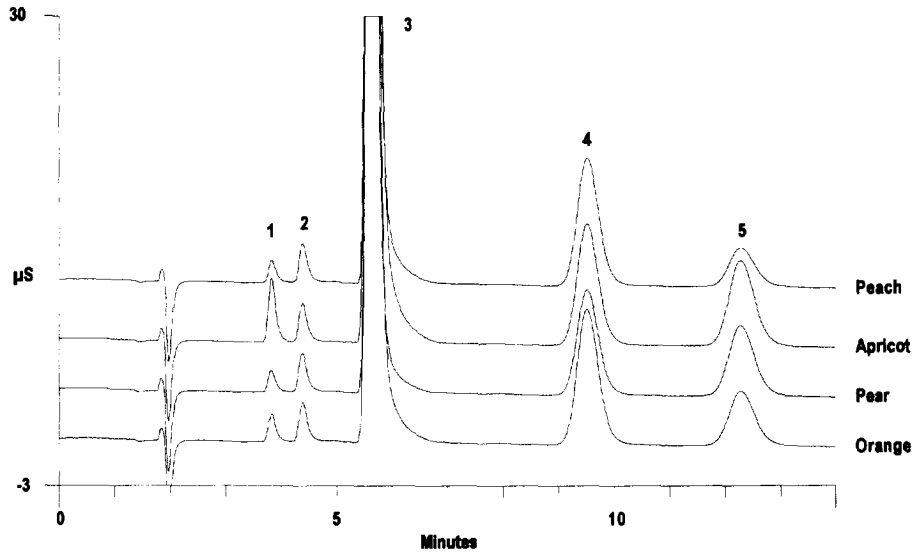

Fig. 2. Typical chromatograms for the determination of cations in different fruit juices and purées. Dilution 1:50 (w/v) for all the samples. Conditions as in Table 1. Peaks: 1 = Na^+; 2 = NH_4^+ (not determined); 3 = K^+; 4 = Mg^{2+}; 5 = Ca^{2+}. Results are summarized in Table 4.

Table 3
Coefficients of IC–AAS regression curves: [IC] = a + b[AAS]

Element	a	b	r
Na	2.778	0.658	0.8705
K	297.1	0.912	0.9494
Mg	7.622	0.892	0.8599
Ca	−5.737	0.924	0.8498

and Table 4. In the sodium distribution plot shown in Fig. 3, the IC data follow the same behaviour as the AAS data. When the sodium concentrations lie in a narrow range such as for orange and peach, the IC response also describes a narrow interval, and when the concentration range is broad, such as for apricot and pear, IC also allows the differences to be measured. An

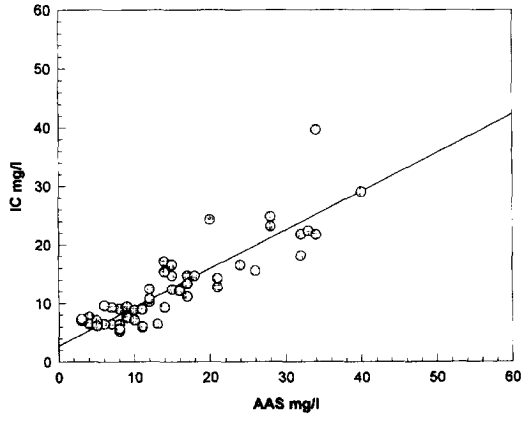

Fig. 3. IC–AAS correlation plot for Na determination.

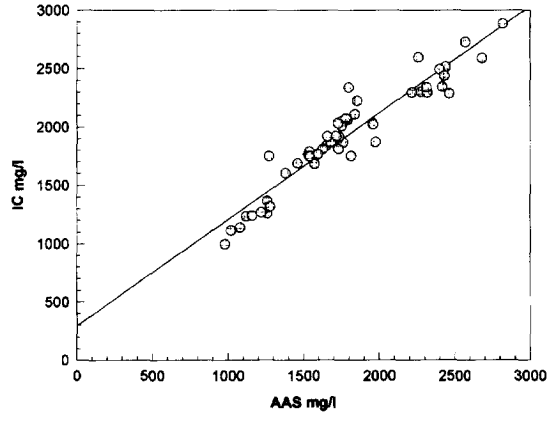

Fig. 4. IC–AAS correlation plot for K determination.

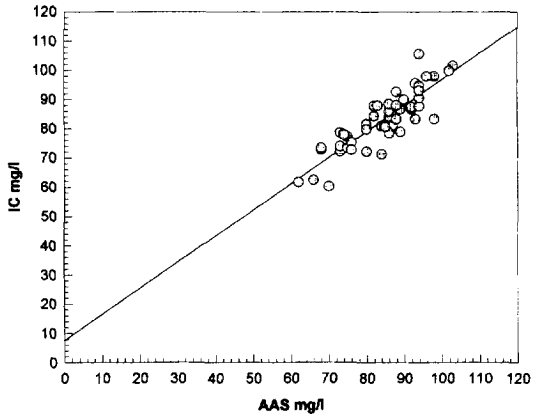

Fig. 5. IC–AAS correlation plot for Mg determination.

analogous behaviour is followed by Mg, as shown in Fig. 5.

The plot for K shown in Fig. 4 suggests that the Ion Pac CS12A column gives a small overestimate for this cation, particularly in the peach sample; however, the case IC results show good precision also for this cation over a broad range of concentrations in the different fruits (K concentrations in apricot range up to 3000 mg/kg, whereas the average K content in pears is as low as 1000 mg/kg).

In the Ca plot it can be seen that the IC data are always lower than the AAS results regardless fruit type; it is evident that dilution of the sample only with water does not allow the complete solubilization of Ca bound to protopectins.

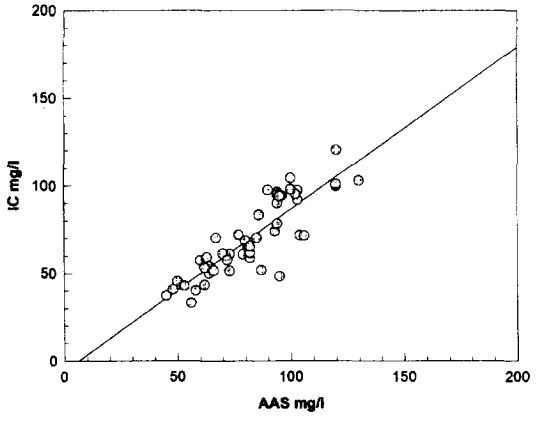

Fig. 6. IC–AAS correlation plot for Ca determination.

In order to confirm this hypothesis, different sample were ashed in a PT crucible, the ash was dissolved in a slightly acidic solution (8 m*M* HCl) and Ca was determined by both AAS and IC. Under these conditions the IC and AAS results were in good agreement with each other, indicating that with IC only free Ca can be determined and it is not possible to determine total Ca by simple dilution of the sample with water.

The data obtained by both IC and AAS are summarized in Table 4; depending on the different cultivars, significant differences in cation content are observed.

Three canonical functions were applied by using discriminant statistical analysis. These functions, whose unstandardized coefficients are reported in Table 5, allow the separation of IC data into different cultivar groups. In detail there is a good separation among apricots, pears and oranges while there is minimum overlap between the peach and orange groups. The discriminant plot in Fig. 7 shows the data separation using the first two of the three functions considered.

4. Conclusions

IC is a technique with high reliability and sensitivity for the determination of Group I and II cations in vegetable matrices, and the regression coefficients show the correlation with AAS data. In addition, IC offers a wide dynamic range and allows the simultaneous determination of all cations of interest plus ammonium ion in less than 15 min, with easy operation and sample preparation.

Another aim of this work was to demonstrate that the IC data for Group I and II cation are analogous to those obtained by AAS and, despite of the differences between the two series of data, for each cation they fall within the ranges recommended by the Code of Practice for the fruit juice industry [2].

For some categories of samples, the presence of other small peaks, well separated but with longer retention times, suggest an overall analy-

Table 4
Comparison between results (mg/l) obtained by IC and AAS

Sample	Parameter	Na		K		Mg		Ca	
		IC	AAS	IC	AAS	IC	AAS	IC	AAS
Orange juice	Min.	6	3	1683	1273	79	69	52	60
	Max.	15	15	2340	1975	106	98	94	112
	Av.	8	9	1871	1684	87	88	67	80
	S.D.	3	4	165	182	8	9	11	15
Peach purée	Min.	6	3	1606	1380	72	68	33	45
	Max.	18	32	2225	1856	89	92	57	105
	Av.	9	11	1934	1690	81	80	46	65
	S.D.	3	7	178	145	5	7	7	17
Apricot Purée	Min.	9	7	2020	1960	73	68	84	86
	Max.	40	34	2883	2820	102	103	120	130
	Av.	19	20	2442	2402	90	90	98	103
	S.D.	8	9	210	201	9	10	8	13
Pear purée	Min.	5	8	997	980	60	62	59	70
	Max.	29	40	1365	1280	80	84	83	106
	Av.	15	22	1215	1153	70	74	69	87
	S.D.	7	10	113	110	7	7	8	12

Table 5
Unstandardized coefficients of discriminant statistical analysis of IC data

Element	Function 1	Function 2	Function 3
Ca	$2.22 \cdot 10^{-2}$	$6.28 \cdot 10^{-2}$	$2.97 \cdot 10^{-2}$
K	$6.63 \cdot 10^{-3}$	$-1.74 \cdot 10^{-3}$	$-1.72 \cdot 10^{-3}$
Mg	$-4.73 \cdot 10^{-2}$	$-1.03 \cdot 10^{-2}$	$1.09 \cdot 10^{-1}$
Na	$-3.22 \cdot 10^{-3}$	$9.62 \cdot 10^{-2}$	$-5.88 \cdot 10^{-2}$
Constant	−9.77	−2.66	−7.60

sis time of 30 min in order to avoid peak overlap. The nature of these spurious peaks is under investigation and they could probably help to increase the information about both the genuineness of samples and the technological processes to which fruit juices are subjected.

The results confirm that cation data obtained by IC can be used to provide suitable parameters for discrimination among different types of vegetable matrices.

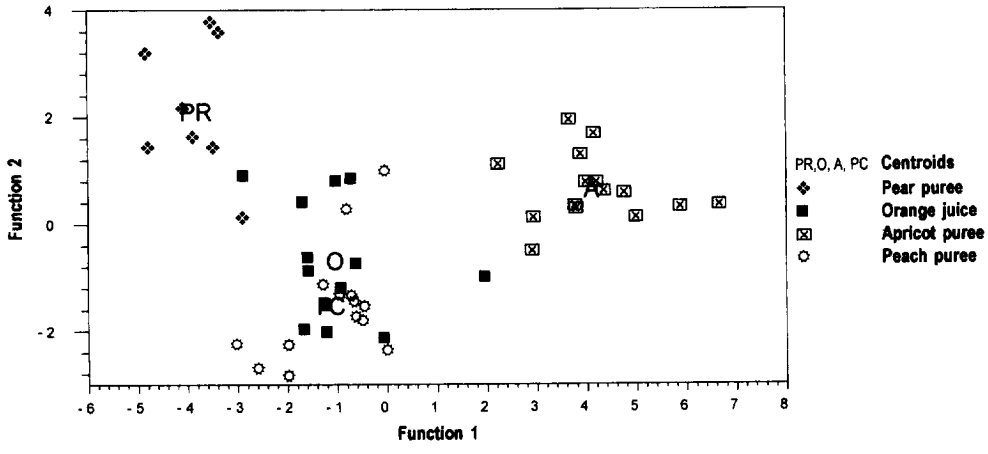

Fig. 7. Discriminant statistical plot obtained using functions 1 and 2 reported in Table 5.

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