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Determination of inorganic anions in commercial seed oils and in virgin olive oils produced from de-stoned olives and traditional extraction methods, using suppressed ion exchange chromatography (IEC)

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Abstract

Ion exchange chromatography (IEC) with a conductivity detector and chemical suppression, was used to evaluate the content of some inorganic anions ($F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}$ and I^-) in commercial seed oils and in Sicilian virgin olive oil samples produced both from whole and de-stoned olives. Anions separation was achieved with a Metrosep Anion Dual 1 column (3.0 × 150 mm; 10.0 μm) packed with quaternary ammonium polymethacrylate. The isocratic elution was carried out using a solution of carbonate (3.12 mM)/hydrogen carbonate (3.25 mM)/2% acetone. Anions were extracted from the oily matrix using hot water pH 8 with carbonate/hydrogen carbonate buffer in an ultrasound bath. Under these conditions, detection limits ranging from 8.4 to 31 $\mu g\ kg^{-1}$ (ppb) were achieved for all the studied anions; the precision of the method was within 6.5 rsd%. The analysis of vegetable oils provided evidence that the concentrations of bromide, nitrite, nitrate and iodide were lower than the detection limits in all the studied samples, whereas chlorides were the most abundant inorganic anions. Furthermore, the concentration of anions was significantly higher in olive oils obtained from the whole fruits than in samples produced from de-stoned olives.

Keywords: Ion exchange chromatography; Inorganic anions; Vegetable oils

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1. Introduction

Vegetable oils are widely used in cooking and alimentary, cosmetic, pharmaceutical and chemical industries; in the last years their consumption has been increasing because of their cholesterol reducing effect, preventing against cardiovascular pathologies. Seed oils are characterized by a high content of poly-unsaturated fatty acids (PUFAs), linoleic and linolenic acids, and α tocopherol, whereas olive oil is high particularly in the mono-unsaturated oleic acid as well as in α-tocopherol (Nestel et al., 1992). In the last years a great importance has been addressed on the monitoring of alimentary products for contamination by heavy metals and inorganic anions, mainly as a result of a requirement of the consumers that are much more concerned today about the quality and the integrity of the foodstuffs then they were in the past. The presence of inorganic elements in vegetable oils depends on many factors as type of soil, climatic condition, fruits maturity, use of pesticides, extraction procedures, storage and technological factors (La Pera & Dugo, 2005, chap. 4). It's important to determinate trace levels of some

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inorganic anions as fluoride, chloride, bromide, nitrate, nitrite, sulphate, or phosphate because they are naturally present in the crude matter and may also be introduced during industrial manipulations (Buldini, Cavalli, & Trifirò, 1997; Buldini, Ferri, & Lal Sharma, 1997; Lopez-Ruiz, 2000). The analysis of inorganic anions in food samples is important from the nutritional, toxicological and technological point of view. A correct daily intake of fluoride is necessary for skeletal bone integrity, but excess consumption causes toxicity (fluorosis). Chloride is one of the most common inorganic anions in foods and in the form of NaCl is employed as preservatives, therefore its determination in foods is essential to fulfil legal regulations and to meet quality control requirements. 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. Of all the studied inorganic anions, bromide nitrite and nitrate were the most important in term of food chain contamination because of their potential toxicity. Bromide was classified by the International Agency for Research on Cancer (IARC) as a carcinogen species for human with renal tumour risks at concentration >0.05 μg/L; moreover intake of excessive bromide can induce a condition termed bromism, with neurological, psychiatric, dermatological, and possibly endocrine effects (van Leewen & Sangster, 1987). High bromide values in vegetable food may derive from soil fumigation with methyl-bromide which is used to combat nematodes, soil-borne fungi, phytophtora, weeds and diseases which attack roots and thus, destroy and kill the plants (Cerutti, 1993, chaps. 3 & 4). Both nitrite and nitrate must also be monitored because of their toxicity: the reduction in the human intestine of nitrate to nitrite can induce metahemoglobinemia and under physiological conditions, nitrite reacts with secondary and tertiary amines forming carcinogenic nitrosamines (Mohri & Scanlan, 1993; Pennington, 1998). Nitrite, as a food additive, serves a dual purpose in the food industry since it both alters the color of preserved fish and meats and also prevents growth of Clostridium botulinum, the bacteria which cause botulism. Sulphates and phosphates are naturally present in living organism; sulphates and phosphates due to their low toxicity they are extensively employed in agriculture particularly as pesticide the former and as fertilizers the latter. The determination of trace inorganic elements in edible fats has always represented a difficult challenge due to the complexity of these matrices. Therefore, opportune sample preparation procedures and sensitive analytical technique are required. The accurate and rapid determination of trace levels of some inorganic cations in vegetable oils using electrochemical methods after concentrated hydrochloric acids extraction, has been widely documented by the authors (Dugo, La Pera, La Torre, & Giuffrida, 2004; Dugo, La Pera, Pollicino, & Saitta, 2003; Dugo, La Pera, Giuffrida, Salvo, & Lo Turco, 2004; La Pera, Lo Coco, Mavrogeni, Giuffrida, & Dugo, 2002; La Pera, Lo Curto, Visco, La Torre, & Dugo, 2002), therefore there is a lack of available data about the analysis of inorganic anions in vegetable oils. Buldini et al. have reported the simultaneous analysis of chloride, phosphate and sulphate in vegetable fat after saponification and UV photolysis by ion exchange chromatography (Buldini, Cavalli et al., 1997; Buldini, Ferri et al., 1997). This paper describes the use of IEC with conductivity detection and chemical suppression for the simultaneous analysis of F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-} and I^- in vegetable oil samples, after extraction with hot water applying ultrasound. Furthermore, this study aims to bring some novelty concerning the inorganic composition of olive oils obtained both from the traditional extraction method (whole olives) and from de-pitted fruits since there are many publications about the influence of stone removing on olive oil quality, with no regard to its inorganic composition (Amirante, 2005; Angerosa, Basti, Vito, & Lanza, 1999; Saitta, Lo Turco, Pollicino, & Dugo, 2003).

2. Materials and methods

2.1. Reagents

Ultra pure sulphuric acid (95–98%) was purchased from Panreac (Barcelona, Spain), and used to prepare a 20 mM solution for the regeneration of the suppressor cartridges. Sodium fluoride; sodium chloride; sodium bromide; sodium nitrite; sodium nitrate; sodium phosphate; sodium sulphate, sodium iodide, sodium carbonate and sodium hydrogen carbonate were purchased from Carlo Erba Reagenti (Milano, Italy). Ultra pure water and acetone (HPLC grade) were purchased from Aldrich Chem. Co. (Milwakee, WI, USA). The samples were filtered through 0.2 μm glass-microfiber GMF Whatman chromatographic filter, before the IEC analysis. Standard olive oil (LGC 7122) purchased from Promochem (Milan, Italy) was used to perform spike-and-recovery test.

2.2. Samples

2.2.1. Seed oils

Commercial refined seed oils produced in Italy were studied. Particularly peanut oils ($n = 5$), sunflower oils ($n = 5$), soy oils ($n = 5$) maize oils ($n = 5$) were analyzed. All the studied seed oils were purchased from a super market on February 2003 and were stored in can.

2.2.2. Olive oils

Olive belonging to Nocellara del Belice variety, harvested in olive groves of the same area near Trapani (Sicily, Italy) during the crop year 2001–2002, were used for experimental tests. Harvesting was done by hand using rakes. An homogeneous batch of olives (about 600 kg) were divided into three lots (A, B, C) and taken to an industrial oil mill where a laboratory mill was used to extract oil. Two lots (A, B) of the de-leafed olives were subjected to stones removing using a suitable tool (de-stoner composed from a cylindrical perforated stationary grill and a rotary shaft), crushed and placed into a water-saving decanter with variable speed of the conveyor, equipped with sensors and automatic adjustment of process parameters: process water volume, oil paste discharge, and differential speed of the conveyor respect to the bowl. Both paste from de-stoned fruit and from the whole fruits were malaxed at 27 °C for 30 min. Lots A, B, and C also differed for the processing water volume added to the paste entering the decanter (expressed as % respect to the pulp weigh), 21.2%, 28.1% and 31.6%, respectively. De-leafed fruits from the lot (C) were submitted, without further treatments, to the extraction process using the same plant. Each lot yielded about 57–59 kg of olive oil which were bottled in dark glass bottles. Particularly 20 samples of olive oil from lots A, 22 from lot B and 25 from lot C were analysed. The studied samples were stored at −20 °C till the analysis.

2.3. Sample extraction procedure

For the chromatographic determination of inorganic anions, a 0.5 g aliquot of oil and 25.0 mL of HPLC grade water (previously subjected to a blank analysis) pH 8 with carbonate (3 mM)/hydrogen carbonate (3 mM) buffer, were introduced in a teflon beaker fitted with PTFE stoppers to avoid sample loss and contamination. The extraction was carried out for about 30 min under magnetic stirring at the temperature of 70 °C. The mixture was then placed in a ultrasonic bath (Soltec, Milan, Italy) operating at the frequency of 50 kHz at 70 °C for 10 min, and after cooling it was centrifuged at 1000 rpm for 5 min; the aqueous phase was directly collected into a 50 mL volumetric flask and the oily one was extracted again as previously described. Aqueous phase was again recovered and added to the first extract, up to the mark with ultra-pure water. In order to remove organic residues, the samples were filtered through 0.2 μm glass-microfiber chromatographic filter, before the IEC analysis. The effect of duration of ultra sound application was studied and the obtained result are given in Table 1.

2.4. Ion exchange chromatographic analysis

Analyses were carried out with a ion chromatograph Compact IC 761 (Metrohm, Switzerland) equipped with a double piston pump, a thermostatted (20 °C) conductivity detector and a continuously regenerable suppressor containing three cartridges which are in turn used for suppression, regenerated with 20 mM H_2SO_4 and rinsed with distilled water. Anions separation was achieved with a Metrosep Anion Dual 1 column (3.0 × 150 mm; 10.0 μm) and ion guard column, both packed with quaternary ammonium polymethacrylate. The isocratic elution was carried out using a solution of carbonate (3.12 mM)/hydrogen carbonate (3.25 mM)/2% acetone. The flow rate was 0.50 mL/min. Samples were injected using a 20 μl loop injector.

Table 1
Recovery from a standard oily mixture containing 10 mg kg^{-1} of each essayed anion after different ultrasound application times

Time (minutes)	F^-	Cl^-	Br^-	NO_2^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	I^-
0	83	92	89	81	88	89	93	86
5	89	98	93	91	98	97	96	93
10	95	103	94	93	101	101	99	95
20	95	101	94	94	102	100	102	96

2.5. Analytical performances

Since edible oil or fat standards certified for inorganic anions were not found in commerce, the performance parameters – precision, accuracy (expressed as recovery factor), reproducibility, and detection limits – were evaluated using a anion free standard olive oil spiked with appropriate amounts of F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-} and I^- sodium salts and let under magnetic stirring overnight in order to obtain a completely homogeneous mixture which was then subjected to the extraction procedure described and analysed by IEC. Fig. 1 shows the chromatogram of standard oily mixture containing 10.0 mg kg^{-1} of each assayed anion (a) and of a virgin olive oil (b). Table 2 reports the retention times, calibration curves, detection limits (S/N = 3), quantification limits (S/N = 10) (Winefordner & Long, 1983), precision, and the recovery factors. Precision was given as the relative standard deviation range of nine measurements at different concentrations levels (0.25, 0.5, 1.0 and 10 mg kg^{-1}) for a total of 36 runs. Furthermore, to verify whether the extraction procedure may cause anion loss, a separate spike-and-recovery test on a virgin olive oil was performed, spiking the sample with appropriate amounts of F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-} and I^- sodium salts, as described earlier; the results are given in Table 3. The reproducibility of the proposed method, expressed as long term stability of the method, was evaluated by extracting and analysing a standard olive oil containing 1.0 mg kg^{-1} of each assayed anion over five consecutive days.

3. Results and discussion

3.1. Analytical method

The determinations of inorganic elements such as fluoride, chloride, bromide, nitrite, nitrates, phosphates and sulphates, in vegetable oils is of great concern both from the technological and the toxicological point of view. Testing for inorganic anions in edible oils has always been very problematic, because they are present in small quantities within a complex organic matrix. Sample preparation is a critical step in the whole analytical procedure. Ion exchange chromatography is the most effective method for anion analysis owing to its precision, high sensitivity, rapidity coupled with the advantage of simultaneous determinations. In 1997, Buldini, Cavalli and Trifirò, developed

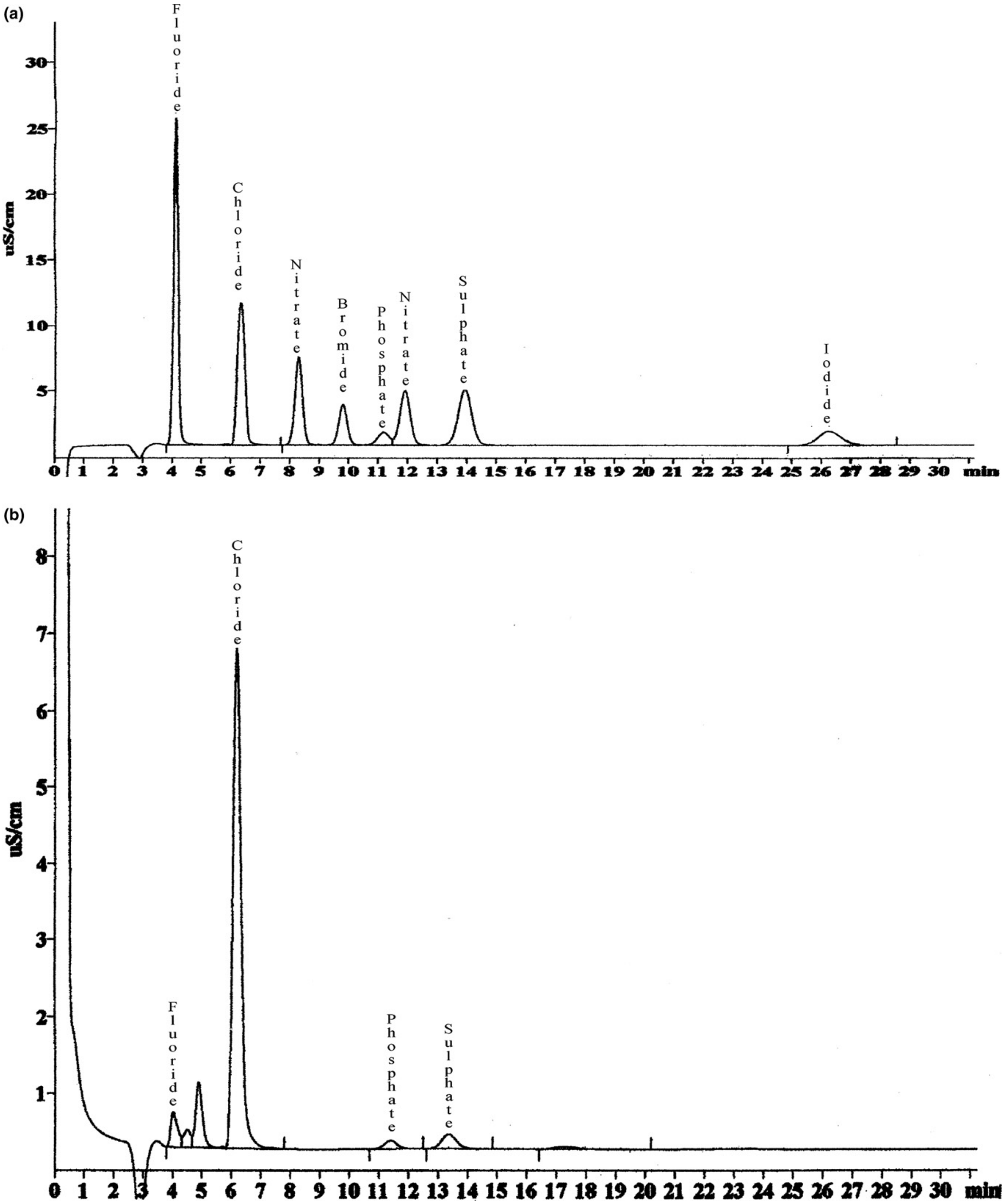

Fig. 1. IEC chromatogram of (a) inorganic anions standard solution containing 10 mg L^{-1} of each essayed anion and of (b) virgin olive oil. Column: Metrosep Anion Dual 1 column (3.0 × 150 mm; 10.0 μm); eluent: carbonate (3.12 mM)/hydrogen carbonate (3.25 mM)/2% acetone; flow rate 0.5 mL/min.

a procedure for the ion chromatographic determination of chloride, phosphates and sulphates in edible vegetable oil; the sample pre-treatment was based on saponification followed by oxidative UV photolysis which took about 3 h. The saponification-photolytic pretreatment was accurate and achieved a high sensitivity, but it did not allow the

Table 2
Calibration curves ($y = Kx$, $r \geqslant 0.999$), detection limits (DL) and quantification limits (QL) for inorganic ions analysis in vegetable oils by ion exchange chromatography

Retention times (minutes)	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	I^-
	4.12	6.77	7.36	8.70	10.47	11.67	14.75	26.24
y	$0.720x$	$1.015x$	$1.656x$	$3.190x$	$1.953x$	$3.130x$	$1.464x$	$3.342x$
rsd%	0.852	1.171	9.170	10.84	4.110	1.927	4.040	0.456
Linearity range (mg kg^{-1})	0–100	0–100	0–100	0–100	0–100	0–100	0–100	0–100
Noise (nS cm^{-1})	7.0	6.0	2.0	1.0	2.5	2.5	3.0	6.0
DL[a] (μg kg^{-1})	9.3	10	8.5	8.4	20.2	29	25	31
QL[b] (μg kg^{-1})	31.1	33.3	28.3	28.1	67.4	96.7	83.3	103.3
Precision (rsd%)[c]	3.7–5.3	3.9–4.2	4.5–6.5	4.3–6.5	4.1–5.0	4.2–6.2	4.1–5.8	4.5–6.5
RF (%)[d]	88–95	96–103	92–94	88–94	92–102	96–102	96–99	88–95

[a] Defined as the signal height at a signal/noise ratio S/N = 3.

[b] Defined as the signal height at a signal/noise ratio S/N = 10.

[c] Precision was expressed as the rsd% range of nine runs performed at different concentrations levels (0.25, 0.5, 1.0, 10 mg kg^{-1}).

[d] Recovery Factor ranges obtained at different concentration levels (0.25, 0.5, 1.0, 10 mg kg^{-1}).

Table 3
Spike and recovery text from a virgin olive oil

	Concentration (mg kg^{-1})	Added (mg kg^{-1})	Expected (mg kg^{-1})	Found[a] (mg kg^{-1})	Recovery%
F^-	1.4	0	1.4	1.25 ± 0.06	89.3
		2	3.4	3.00 ± 0.13	91.2
		5	6.4	6.00 ± 0.25	93.0
Cl^-	17	0	17	16.10 ± 0.7	94.7
		10	27	25.90 ± 1.0	95.9
		20	37	36.20 ± 1.5	97.8
Br^-	<	0	0	0	–
		0.5	0.5	0.43 ± 0.03	86.0
		2	2	1.75 ± 0.11	87.5
NO_2^-	<	0	0	0	–
		0.5	0.5	0.44 ± 0.03	88.0
		2	2	1.81 ± 0.12	90.5
NO_3^-	<	0	0		–
		0.5	0.5	0.46 ± 0.04	92
		2	2	1.90 ± 0.14	95
PO_4^{3-}	2.5	0	2.5	2.30 ± 0.14	92.0
		5	7.5	7.11 ± 0.46	94.7
		10	12.5	12.20 ± 0.73	97.6
SO_4^{2-}	3.1	0	3.1	2.97 ± 0.15	95.8
		5	8.1	7.85 ± 0.39	96.9
		10	13.1	12.68 ± 0.64	96.8
I^-	<	0	0	0	–
		0.5	0.5	0.44 ± 0.03	88.0
		2	2	1.87 ± 0.15	93.5

[a] Mean of three analysis.

determination of fluoride, nitrate and iodide. This paper describes the use of IEC with conductivity detection and chemical suppression, for the simultaneous analysis of fluoride, chloride, bromide, nitrite, nitrate, phosphate, sulphate and iodide in vegetable oil after extraction in a pH 8 carbonate/hydrogen carbonate buffered solution at 70 °C, applying ultrasound. This extraction procedure employs the principles of traditional solvent extraction, exploiting the greater affinity of inorganic anions towards an aqueous medium respect to an oily one. The effect of ultrasound is to help penetration of the solvent in the sample matrix and to promote the dissolution of the inorganic anions in the aqueous phase; Table 1 provides evidences that the application of ultrasound for 10 min. ensures good recoveries. The high sensitivity of the proposed method allow to determine anions concentration lower than 30 μg kg^{-1}; the precision of the method is within 6.5% (expressed as rsd% of nine runs) whereas accuracy ranged from 88% to 102% (expressed as recovery factor at different concentration levels) (Table 2). The recovery test from a virgin olive oil shows that anions quantification remained unaffected by extraction treatment followed by filtration on a carbon column: mean obtained recoveries spanned from 88% to 97.6% (Table 3). Reproducibility, which is very important when establishing routine methods to be used over extended periods, obtained for F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-} and I^- IEC analysis was 94%, 99%, 94%, 91%, 99%, 95%, 95% and 91%, respectively. This method couples rapidity with high performances, therefore, is suitable for routine analysis.

3.2. Analysis of seed oils

The analysis of F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-} and I^- were performed in commercial seed oils samples using the proposed ion chromatographic method. The obtained results (Fig. 2) provided evidence that the concentrations of bromide, nitrite, nitrate and iodide were lower than the detection limits in all the studied seed oils. Chloride were the most abundant inorganic anions, mean concentrations ranging from 1 to 6.5 mg kg^{-1} were found, whereas fluoride, phosphates and sulphates mean levels were lower than 1 mg kg^{-1} in all the analysed seed oils. On the whole, even though legal limits for anions concentration in edible vegetable oils has not yet been established, the obtained results has evidenced very low anions contamination levels in Italian commercial seed oils, therefore their consumption does not represent a risk for human health.

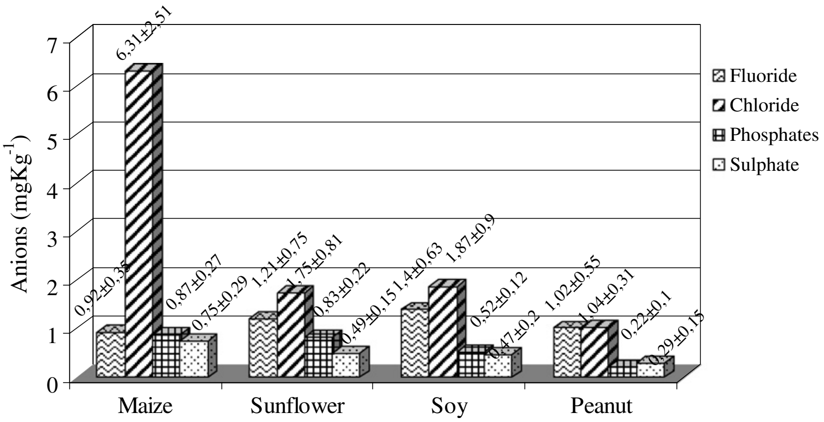

Fig. 2. Average levels of inorganic anions in commercial seed oils.

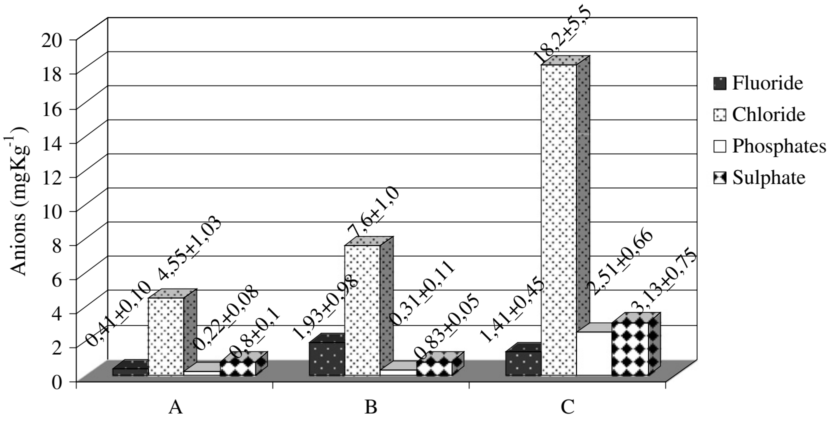

Fig. 3. Average levels of inorganic anion in olive oil samples from Nocellara del Belice variety produced from de-stoned olives (A and B) and from whole fruits (C).

3.3. Analysis of olive oils

Olive oil is the most important fat of Mediterranean diet and in the last years its production and consumption was increased worldwide. Olive oil production technology has been modified in the last decades in order to improve olive oil quality. Some researches about the influence of de-stoning the olives on oil composition and quality were carried out (Angerosa et al., 1999; Saitta et al., 2003).To verify whether the concentration of inorganic anions in virgin olive oils was influenced by the olive fruit stone, oils from whole olives and from pulp-only tissue, respectively, were submitted to ion exchange chromatographic analysis using the method described. Fig. 3 shows that the content of chloride, phosphates and sulphates was significantly higher in oils obtained from the whole fruits (lot C), indicating that the stone contribute to the presence of inorganic anions in the oil more than the pulp tissue. Among the oils obtained from de-stoned fruits, those extracted using the highest amount of processing water (lot B) had a higher content of fluoride, chloride, phosphates and sulphates giving evidence that water volume added to the paste affect inorganic anions levels in olive oils.

4. Conclusion

Literature reports few data about the presence of inorganic anions in edible oils since their determination in fats has always been very problematic, because they are present in small quantities within a very complex organic matrix. This paper describes a study regarding the ion chromatography determination of several inorganic ions by conductivity detection and chemical suppression in moderately alkaline solutions after aqueous extraction with buffered CO_3^{2-}/HCO_3^- at pH 8 in a ultrasound bath. This method couples rapidity with high precision accuracy and sensitivity, therefore, is suitable for routine analysis. The analysis performed on commercial seed oils and on olive oils gave evidence that chloride were the most abundant inorganic anions, followed by fluoride, phosphates and sulphates; bromide, nitrite, nitrate and iodide were not detected. The method described was further used to assess the effect of olive-stone removing on inorganic anions concentration in olive oils. The obtained results have shown that the content of chloride, phosphates and sulphates was significantly higher in oils obtained from the whole fruits, indicating that the stone contribute to the presence of inorganic anions in the oil more than the pulp tissue.

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