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VALORISATION OF APPLE PEELS

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Abstract

The peels of processed apples can be recovered for further food applications. Limited information on the valorisation of this type of waste is available for cooking varieties, e.g. cv Bramley's Seedling. Extracts from fresh or dried (oven-dried or freeze-dried) peels were obtained with solvents of different polarity (aqueous acetone or ethanol) and assayed for their total phenolic content and antioxidant capacity; their antiradical power was compared to herb extracts. The dried peels were also characterised as bulk powders by assessing their nutritional value and total phenolic content. High amounts of ascorbic acid (up to 4 mg/g, dry weight) and polyphenols (up to 27 mg gallic acid equivalents/g, dry weight) were found in the peels, with the latter contributing significantly to the antioxidant capacity; the nutrient profile was low in

protein (less than 10%, w/w) and total dietary fibre content (less than 40%, w/w). Higher yields of phenolic antioxidants were recovered with acetone from freeze-dried peels; the resulting extracts had equivalent antioxidant power to oregano leaves (*Origanum vulgare* L.). The combination of oven-drying/ethanol led to lower recovery yields of phenolic antioxidants; however, these conditions could increase the feasibility of the extraction process, leading to antioxidant extracts with lower energy or cost input, and higher suitability for further food use. The recovery of phenolic antioxidants from the peels of processed apples could be a valuable alternative to traditional disposal routes (including landfill), in particular for cooking varieties. The recycling process could enhance the growth of traditional culinary apple markets in UK and Ireland thanks to the new business opportunities for the peel-derived materials.

Keywords: waste valorisation; cooking apples; peel polyphenols; antioxidant value.

1 INTRODUCTION

There is an increasing interest about natural plant extracts (i.e. botanicals) in novel food applications, as nutraceutical ingredients or natural preservatives and antioxidants (Coppens et al., 2006; Decker et al., 2010; Medina et al., 2003; Naidu et al., 2000; Pazos et al., 2005). Various agri-food waste and by-products have been screened for the recovery of natural phenolic antioxidants (Moure et al., 2001). The recovery of valuable materials is a strategy of waste minimisation (Bates, Phillips, 1999). Some nutraceutical products have been developed from grape waste or apple peels, and marketed for the functional markets of Japan and U.S.A. (Shoji et al., 2004; Yamakoshi et al., 2002). In Europe, the use of botanicals such as vegetable

and fruits, herbs and spices, herbal teas and infusions, and herbs is allowed in food and beverages for taste or functional purposes (e.g. guarana, gentian, etc.) (Coppens et al., 2006); however, the functional applications of many botanicals have not yet received the scientific opinions of the European Food Safety Authority (EFSA) (Gilsenan, 2011).

Apples are important dietary sources of phenolic compounds and have strong antioxidant capacity compared to other fruits (Sun et al., 2002). Apple polyphenols have various *in vitro* bioactivities, possibly in combination with dietary fibre (i.e. reduced risk of coronary heart disease) (Boyer, Liu, 2004). Higher amounts of polyphenols, in particular flavonol glycosides, are generally found in the skin of the fruit, compared to the pulp (Khanizadeh et al., 2008). Some studies have reported about the recycling of apple peels as a source of phenolic compounds and/or dietary fibre; depending on the compounds, different peel waste-derived materials were developed (Table 1).

The apple peels were preferably processed into a dried and pulverised bulk material for fibre formulation or nutraceutical use. Phenolics were extracted with organic solvents (or aqueous mixtures thereof) and then characterised for their potential health benefits. The second recycling option involved the preparation crude or purified mixtures of phenolic antioxidants and/or their formulation in nutraceutical or functional food applications. To the best of our knowledge, the preparation and characterisation of apple peel extracts for food stabilisation or preservation has not been studied.

1 **Table 1** Recycling of apple peel-derived materials: processing conditions (drying; extraction solvent); target compounds;
 2 and further applications.

<i>Peel-derived materials</i>	<i>Preservation conditions (peel material)</i>		<i>Extraction solvent (phenolic compounds)</i>	<i>Applications</i>	<i>Target compounds</i>	<i>References</i>
	<i>Pre-drying treatments</i>	<i>Drying</i>				
	N/A	Drum-drying;	70% Acetone (v/v)	Fibre formulation/ Functional foods	Dietary fibre and phenolic compounds	(Henríquez et al., 2010)
<i>Bulk peel powders</i>	Water blanching;	Oven-drying (60°C, with air circulation)	Methanol	Fibre formulation/ Functional foods	Dietary fibre and phenolic compounds	(Rupasinghe et al., 2008)
	Water blanching; ascorbic acid dip	Freeze-drying; air-drying; oven-drying (at 40/60/80°C, no air circulation)	80% Acetone or 80% ethanol (v/v)	Nutraceuticals	Phenolic compounds	(Wolfe, Liu, 2003)
	N/A	Freeze-drying	Methanol	Functional foods	Phenolic compounds	(Huber, Rupasinghe, 2009)
<i>Antioxidant peel extracts</i>	N/A	N/A	N/A	Functional foods	Phenolic compounds	(Wegrzyn et al., 2008) ^a
	N/A	N/A	Ethanol or methanol	Nutraceuticals	Phenolic compounds	(Tanabe et al., 1994)
	N/A	Freeze-drying	80% Acetone (v/v)	Nutraceuticals	Phenolic compounds	(Wolfe et al., 2003)

3 ^a In this study, the apple peel extract was commercially available; the conditions used for its preparation were not described. N/A: not applicable.

4 In the preparation and characterisation of plant waste-derived materials, conditions such as the
5 drying and the liquid extraction of phenolic compounds have an impact onto the feasibility of
6 the recycling process (i.e. energy consumption and cost input), and further applications of the
7 recovered ingredient (Peschel et al., 2006). For example, the extracts from apple peels
8 developed by Huber, Rupasinghe (2009) were obtained with methanol; therefore they could
9 not be tested in food systems. Ethanol and water should be preferred over methanol in view of
10 food applications (Spigno et al., 2007). Freeze-drying, which is advantageous for heat
11 sensitive materials, also requires higher energy consumption and initial and maintenance costs
12 than oven-drying or air-drying, therefore its use could be limited in the industry (Cieurzyńska,
13 Lenart, 2011).

14 The diversion of the peel waste from traditional disposal routes (landfertilising, feedstock, or
15 landfill) towards more valuable food applications could favour the sustainable development of
16 the culinary apple markets in the British Isles that are primarily based on cv Bramley's
17 Seedling. This variety is known for the sole purpose of cooking, i.e. processed into sauce or
18 puree, or used for home baking. Due to changes in the lifestyle, at the end of the 90's the fresh
19 sector has narrowed in UK (Carter, Shaw, 1993); the same trend has occurred in Ireland, with
20 the consequent overproduction at low farm gate prices (Bord Glas, 2003). In the absence of
21 official statistics about the waste generated, it was estimated that 300 tonnes of peels could be
22 discarded annually by processing lines in Ireland (Bord Bia, 2008), assuming a yield of 11%

23 (w/w) of peels from the whole apple. Another 5,000 tonnes of peels could be generated from
24 the amount of processed lines in UK.¹

25 The peels and/or pulp of cooking apples were assessed for their phenolic content in order to
26 establish their dietary significance (Imeh, Khokhar, 2002; Price et al., 1999). However, few
27 studies have investigated their recovery for valuable applications. Polyphenols were extracted
28 from the pomace as potential nutraceutical compounds (McCann et al., 2007). The
29 contribution of the skin to the extractable phenolics from the pomace was studied in
30 comparison to the peeled fruit, distinguishing among soluble and insoluble bound components
31 in view of further applications (Massini et al., 2010).

32 In the present study, different approaches for the preparation of peel-derived materials (bulk
33 powders or extracts) with nutritional and/or antioxidant value from cv Bramley's Seedling
34 apple (origin: Ireland) were investigated with the aim of establishing an optimal recovery
35 process for further food use. The recycling value of these materials was compared to other
36 plant-based products already developed for food applications (i.e. from the peels of different
37 apple varieties; or herb leaves). Processing conditions (drying and/or extraction solvent) with
38 different energetic or cost input were compared with the aim of defining a feasible recycling
39 process with increased industrial applications. This valorisation approach could be applied to
40 other processed apples in order to increase the type of waste-derived products recovered from
41 solid fruit waste.

¹ <http://www.bramleyapples.co.uk>

42 2 MATERIALS and METHODS

43 2.1 CHEMICALS

44 Chemicals were purchased from Sigma-Aldrich (Ireland) and included: sodium nitrite; sodium
45 carbonate; ferric chloride; aluminium chloride hexahydrate; 2.0 N Folin-Ciocalteu's phenol
46 reagent; 2,4,6-tri(2-pyridyl)-s-triazine (TPTZ); 2,2-diphenyl-1-picrylhydrazyl (DPPH); Celite,
47 acid-washed; enzymes for the digestion of the dietary fibre: amyloglucosidase from
48 *Aspergillus niger*; protease from *Bacillus licheniformis*; α -amylase (heat stable) from *Bacillus*
49 *licheniformis*; and the standards: (+)-catechin hydrate; gallic acid and L-ascorbic acid.

50 2.2 PLANT MATERIAL

51 Two batches of apples (i.e. 3-5 kg per batch) (*Malus domestica* Borkh. cv. Bramley's
52 Seedling) were purchased from a local store (Dublin, Ireland) between October 2007 and April
53 2008. According to the information provided by the retailer, the apples were grown in Co.
54 Armagh, Northern Ireland, harvested in late August/September and made available throughout
55 the year thanks to storage facilities (under controlled atmosphere).

56 The purchased apples were stored at 4°C in a polyethylene film, until processing. The apples
57 were washed under tap water, dried by patting on a paper cloth and weighed. The peels were
58 manually removed with a hand-peeler. Five grams of fresh peels were collected in triplicate
59 from each batch of apples and immediately assayed. The remaining peels were oven-dried at
60 60 ± 2 °C (OD) on stainless steel trays in a ventilated oven (Weiss Gallenkamp BS Oven 250,
61 UK) or freeze-dried (FD) in a Micro Modulyo E-C Apparatus (Davidson & Hardy, USA) until

62 a constant weight was achieved, in the dark. After drying, the samples were pulverised in a
63 coffee grinder and the resulting powders were stored in amber bottles at -20°C until analysis.

64 2.3 *EXPERIMENTAL DESIGN*

65 The experimental design included the preparation of peel extracts from oven-dried samples
66 with 80% ethanol, or freeze-dried peels with 80% acetone. The drying and solvent systems
67 were studied under these combinations (i.e. freeze-drying/acetone; and oven-drying/ethanol)
68 with the purpose of comparing conditions with less or more favourable impact onto the
69 feasibility of the recovery process. The resulting extracts were compared to fresh samples
70 extracted under similar conditions in order to assess the effect of processing onto the phenolic
71 content and antioxidant capacity of the peels. Oregano and rosemary leaf extracts were
72 prepared from herbs purchased from a local store and used as reference plant extracts with
73 established food applications (Naidu, 2000).

74 The dried and pulverised peels were also characterised as bulk materials (i.e. nutritional value
75 and total phenolic content). Soluble phenolic compounds were extracted with acetone or
76 ethanol from dried peels (oven-dried or freeze-dried) and further quantified. The colour and
77 free acidity of the powders were assessed because of their potential sensorial impact in further
78 food formulation.

79 2.4 CHARACTERISATION OF BULK PEEL POWDERS

80 2.4.1 Proximate analysis

81 The proximate analysis was carried out according to official methods (AOAC, 2000): moisture
82 content (Method 930.04); ash content (Method 930.05); protein content (Method 920.152); fat
83 content (Method 983.23, with petroleum ether); ascorbic acid content (Method 967.21). The
84 total dietary fibre (TDF) was determined according to Prosky et al. (Prosky et al., 1985).
85 Sugars were extracted from the plant matrix using 80% ethanol (v/v) under boiling conditions
86 and quantified as glucose equivalents (g/100 g) using the phenol-sulphur method by Dubois et
87 al. (Dubois et al., 1956). The analyses were done in triplicate and expressed on a dry weight
88 basis (DW).

89 2.4.2 Free titratable acidity

90 For the free titratable acidity, 1 g of peel powder was boiled for 10 mins in 20 mL of distilled
91 water and filtered through a Büchner funnel. The free titratable acidity was measured
92 according to AOAC (2000) (Method 942.15.b).

93 2.4.3 Colour

94 The CIELAB* colour (L*; a*; b* values) of the powders was measured in triplicate using
95 ColorQuest®Xe (HunterLab, USA) applying the reflectance method: 10° observer; D65
96 illuminant. The instrument was calibrated with standard white and black tiles. The colour
97 values were expressed as: L* = lightness (from 0 to 100); a* = redness/greenness (from +a* to
98 -a*); b* = yellowness/blueness (from +b* to -b*).

99 2.5 CHARACTERISATION OF PEEL EXTRACTS

100 2.5.1 Extraction of phenolic compounds

101 Crude mixtures of soluble polyphenols were obtained in triplicate from fresh or dried peels,
102 using a procedure previously described with minor modifications (Wolfe, Liu, 2003). For the
103 dried peels, ~1 gram of powder was homogenised (ULTRA-TURRAX T25, IKA Labordeck,
104 Germany) with 40 g of chilled aqueous 80% ethanol or 80% acetone (v/v) at 9500-13500 min⁻¹
105 for 5 min. The obtained slurry was filtered under vacuum. The remaining solids were added
106 to 15 mL solvent and extracted again, homogenising for 1 min. For the fresh peels, 5 g of
107 sample was blended in a portable mini blender (dj2000 Illico Mini Chopper, Moulinex,
108 France) with 40 g of solvent for 3 min, and then filtered through N.6 Whatman paper in a
109 Büchner funnel. In the last filtration step, for both fresh and dried samples, another 15 mL of
110 solvent was poured onto the filter cake. During the extraction, the extracts were kept chilled in
111 an ice bath, in the dark. Homogenisation was stopped after one minute, waiting at least another
112 minute before resuming. The filtrates were collected and the organic solvent was removed at
113 40°C using a Büchi rotavapor, until the aqueous phase remained. The concentrated extracts
114 were brought to the volume of 25 mL with distilled water, filtered through N.1 Whatman
115 paper, and stored at -20°C in the dark. Before analysis, they were thawed, centrifuged at 8,000
116 rpm for 15 min, filtered through 0.45 µm PTFE (Acrodisc, Pall, UK) membrane disc filter, and
117 brought up to the volume of 50 mL with distilled water.

118 *2.5.2 Total phenolic content*

119 The total phenolic content (TPC) was assessed using Folin-Ciocalteu assay (Singleton et al.,
120 1999). Volumes of 0.5 mL of distilled water and 0.125 mL of sample were added to a test
121 tube. A volume of 0.125 mL of 2.0 N Folin-Ciocalteu reagent was added and allowed to react
122 for 6 min. Then, 1.25 mL of a 7% sodium carbonate solution (v/v) was added to the mixture
123 and allowed to stand for 90 min in the dark, for colour development. Before reading the
124 absorbance at 760 nm in a spectrophotometer (Spectronic 1201, Milton Roy, USA), the
125 mixture was diluted up to 3 mL with distilled water. Gallic acid solutions were used for the
126 standard calibration curve and the total phenolic content was expressed as mg gallic acid
127 equivalents (GAE)/g or 100 g peels (dry weight or fresh weight basis, DW or FW). All
128 measurements were carried out in triplicate.

129 *2.5.3 Total flavonoid content*

130 The total flavonoid content (TFC) was assessed using aluminium-chloride assay (Zhishen et
131 al., 1999). A volume of 0.25 mL of sample was added to a test tube containing 1.25 mL of
132 distilled water. An aliquot of 0.075 mL of 5% sodium nitrite solution (w/v) was added to the
133 mixture and allowed to stand for 5 min. Then, the addition of 0.15 mL of 10% aluminium
134 chloride (w/v) developed a yellow flavonoid-aluminium complex. After 6 min, 0.5 mL of
135 4.3% NaOH (w/v) was added. The absorbance was measured immediately in a
136 spectrophotometer (Spectronic 1201, Milton Roy, USA) at 510 nm and compared to a
137 standard curve of (+)-catechin solutions. The flavonoid content was expressed as mg catechin
138 equivalents (CE)/g peels (FW). All measurements were carried out in triplicate.

139 *2.5.4 Ferric reducing antioxidant power*

140 The antioxidant capacity was evaluated using a modified FRAP assay procedure based on a
141 previously published protocol (Stratil et al., 2006). A freshly prepared FRAP-reagent (25 mL
142 acetate buffer, 300 mM, pH 3.6 + 2.5 mL 10 mM TPTZ (2,4,6-tripyridyl-5-triazine) in 40 mM
143 HCl + 2.5 mL 20 mM FeCl₃·6 H₂O) was heated in water bath at 37°C for 5 min before being
144 transferred (0.9 mL) into tubes containing 0.1 mL of plant extracts. The tubes were left in
145 water bath at 37°C for 40 minutes. The absorbance was then measured at 593 nm in a
146 spectrophotometer (Spectronic 1201, Milton Roy, USA). The antioxidant capacity was
147 compared to standard L-ascorbic acid through a calibration curve, and expressed as mg
148 ascorbic acid equivalents (AAE)/g peels (FW), which was also referred to as AEAC (Ascorbic
149 acid Equivalent Antioxidant Capacity). All measurements were carried out in triplicate.

150 *2.5.5 Radical scavenging capacity*

151 The radical scavenging capacity against a synthetic radical compound (DPPH[•]) was measured
152 according to Makris et al. (2007), with some modifications. A volume of 0.1 mL of diluted
153 extracts (bulk; 1:2; 1:5; 1:10; 1:20; 1:50) was added in a reaction vessel containing 0.9 mL of
154 a freshly prepared DPPH[•] solution (0.08 mM in 96% ethanol, v/v); the reaction was allowed to
155 run for at least 30 minutes. The decrease in absorbance of the samples was read at 515 nm
156 against a blank of distilled water in a spectrophotometer (Spectronic 1201, Milton Roy, USA)
157 and compared to that of a control solution of DPPH[•] prepared with 0.1 mL of distilled water.

158

159 The % Reduced DPPH[•] was calculated using the following equation:

160

$$\% \text{ Reduced DPPH}^{\bullet} = [(1 - \text{Abs sample})/\text{Abs control}] * 100$$

161

162 The % Reduced values were expressed as AEAC (mg AAE/g peels, FW) by comparison with

163 a standard calibration curve with ascorbic acid. The IC₅₀ value (i.e. concentration of plant

164 extract that reduces by 50% the initial concentration of the radical form of DPPH[•] in the

165 reaction mixture) was calculated from the curves of sample concentration (as mg/mL, FW) vs.

166 % Reduced DPPH[•]. The values were expressed as Antiradical Power (ARP) = 1/IC₅₀ (mL/g

167 sample, FW) according to Brand-Williams et al. (1995). For the preparation of plant extracts

168 with reference antiradical power, fresh leaves of oregano (OR) and rosemary (ROS) were

169 purchased from a local store (Dublin, Ireland) and oven-dried at 60°C ± 2°C in a ventilated air

170 oven (Weiss Gallenkamp BS Oven 250, UK) until constant weight was achieved, in the dark.

171 The samples were pulverised using a mortar and a pestle. Rosemary (5 g) and oregano (2 g)

172 leaf powders were extracted with 95% ethanol (v/v) homogenising for 2 minutes, according to

173 the method described by Almeida-Doria, Regitano-d'Arce (2000). The resulting ROS and OR

174 extracts were filtered through N°6 Whatman filter paper using a Büchner funnel, under

175 vacuum. The filtrates were collected and further evaporated in a rotary evaporator at 40°C

176 under vacuum, until 20% of the original volume remained. The extracts were stored in amber

177 glass bottles at -20°C until analysis.

178 2.6 *STATISTICAL ANALYSIS*

179 Statistical analysis was conducted using StatGraphics Centurion XV (Statpoint Technologies
180 Inc., USA) and GraphPad v. 5.01 for Windows (GraphPad Software Inc., USA). Normal data
181 was tested for significance using the one-way ANOVA (LSD post-hoc test), and F-test as
182 appropriate. A regression analysis was also carried out. For all the statistical tests, the
183 significance level taken was $p < 0.05$.

184

185 **3 RESULTS and DISCUSSION**

186 *3.1 BULK PEEL POWDERS*

187 The characteristics of the powders obtained under different drying conditions were studied and
188 further compared (Table 2). Regardless of the drying method, the powders generally had
189 reduced protein content (less than 5%), making them a poor animal feed. They had high
190 content of total carbohydrates (up to 80%, w/w). When compared to peel materials already
191 developed from dessert varieties, e.g. cv Granny Smith (Henríquez et al., 2010), cv Northern
192 Spy or cv Ida Red (Rupasinghe et al., 2008), the powders from Bramley apple peels had lower
193 total dietary fibre (less than 40%, w/w, DW). They also had high acidity (almost 4-fold higher
194 than in the peels of cv Granny Smith), which could negatively impact the sensorial
195 characteristics in further food formulations. The ascorbic acid content was high, with values
196 ranging from 3.0 to 4.4 (mg/g, DW); Łata (2007) reported values of 0.7–3.4 mg/g in the peels
197 of various dessert apples.

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199
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Table 2 Physical and chemical characteristics of bulk peel powders as affected by the drying method

<i>Parameter</i> (%, w/w)	<i>Drying method</i>	
	<i>OD</i>	<i>FD</i>
Total ash	2.23 ^a ± 0.10	2.49 ^a ± 0.44
Total fat	3.83 ^b ± 0.23	6.61 ^a ± 0.82
Total protein	5.07 ^a ± 0.32	5.36 ^a ± 0.19
Total dietary fibre	35.38 ^a ± 2.22	32.49 ^a ± 0.10
Total sugars (as glucose)	46.00 ^a ± 8.27	40.36 ^a ± 3.03
Free titratable acidity (% malic acid, w/v)	8.52 ^a ± 0.11	8.16 ^a ± 0.76
Ascorbic acid (mg/g)	3.01 ^b ± 0.30	4.42 ^a ± 0.20
<i>Colour</i>		
L*	71.3 ^b ± 0.6	74.3 ^a ± 0.2
a*	1.9 ^a ± 0.2	-6.6 ^b ± 0.1
b*	30.5 ^b ± 0.3	34.6 ^a ± 0.1

201 Values were expressed as mean ± SD (n = 6) on a dry weight basis, considering an average residual moisture
202 content of 7.5% and 9.0% for oven-dried (OD) and freeze-dried (FD) peels, respectively. Different superscript
203 letters in each row denoted significant difference (p<0.05) between samples.
204

205 Some physical and chemical parameters were significantly affected by the drying system
206 (Table 2). In particular, the thermal drying (e.g. oven-drying) produced a significant reduction
207 of the fat and ascorbic acid content of the powders in comparison to freeze-drying. The oven-
208 dried powders poorly retained the colour of the fresh peels in comparison to freeze-dried
209 samples, and their colour had significant (p<0.05) lower greenness and yellowness values.
210 The drying system also influenced significantly (p<0.001) the yield of total phenolic
211 compounds (calculated as TPC) in the final powders (Table 3). The yield also depended on the
212 organic solvent used for their extraction (p<0.001). The thermal decomposition of the lipid
213 substances in the skin could be associated to an increased oxidative damage of its natural
214 antioxidants.

215 **Table 3** **Total phenolic content of oven-dried and freeze-dried bulk peel powders**
 216 **(extracted with different organic solvents).**

<i>Drying system</i>	<i>Extraction solvent</i>	<i>Total phenolic content (mg GAE/g, DW)</i>
Freeze-drying (FD)	Acetone (Ac)	27.04 ± 1.76
	Ethanol (Et)	21.93 ± 0.36
Oven-drying (OD)	Acetone (Ac)	21.75 ± 0.36
	Ethanol (Et)	17.97 ± 0.42
<i>F-test</i>		
<i>Main effects</i>	LSD _{0.05} = 1.24	<i>Mean</i>
Drying system	***	24.97 (FD)
		20.04 (OD)
Extraction solvent	***	24.78 (Ac)
		20.23 (Et)

217 *** indicated a highly significant effect (p<0.001). TPC values were expressed as mean ± SD (n = 6). GAE:
 218 gallic acid equivalents.

219
 220

221 The loss of phenolic compounds during oven-drying was reported in various plants by
 222 different authors (Moure et al., 2001). Natural antioxidants are normally accumulated in the
 223 skin in order to supply their antioxidant protection (Łata, 2007). According to Chinnici et al.
 224 (2004), phenolics could be regenerated by non-enzymatic reactions with ascorbate in the apple
 225 fruit. The TPC values of the Bramley apple peels were in agreement with results already
 226 reported for this variety by Imeh, Khokhar (2002).

227 3.2 PEEL EXTRACTS

228 3.2.1 Phenolic yield

229 The total phenolic (TPC) and flavonoid (TFC) contents of fresh and dried peels extracted with
 230 different solvents were compared (Table 4). With regard to the same solvent, dried peels had
 231 similar TPC than fresh samples, but their TFC was significantly different (p<0.05).

232
233

Table 4 Phenolic content and antioxidant capacity of fresh and dried peels extracted with the same type of solvent.

<i>Parameter (mg/g peels, FW)</i>	<i>Extraction solvent</i>	<i>Peels</i>	
		<i>Fresh</i>	<i>Dried¹</i>
<i>TPC (as GAE)</i>	Acetone	7.68 ^a ± 0.74	7.63 ^a ± 0.17
	Ethanol	6.35 ^b ± 0.76	5.86 ^b ± 0.35
<i>TFC (as CE)</i>	Acetone	5.34 ^a ± 0.48	4.51 ^b ± 0.10
	Ethanol	4.76 ^b ± 0.47	4.03 ^c ± 0.06
<i>FRAP (as AEAC)</i>	Acetone	13.26 ^a ± 0.88	13.92 ^a ± 0.29
	Ethanol	9.88 ^b ± 1.66	10.43 ^b ± 1.34
<i>Radical scavenging capacity (DPPH) (as AEAC)</i>	Acetone	12.11 ^a ± 1.22	10.43 ^b ± 1.34
	Ethanol	9.15 ^c ± 0.61	7.27 ^d ± 0.64

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¹ Freeze-dried (extracted with acetone); oven-dried (extracted with ethanol).

Values were expressed as mean ± SD (n = 6). Different superscript letters indicated significant difference (p<0.05) between fresh and dried samples extracted with the same type of solvent (within row). TPC: total phenolic content, expressed as gallic acid equivalents (GAE); TFC: total flavonoid content, expressed as catechin equivalents (CE); FRAP: ferric reducing antioxidant power, expressed as ascorbic acid equivalents (AEAC); Radical scavenging capacity against DPPH, expressed as ascorbic acid equivalents (AEAC).

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These findings suggested that some flavonoids were lost during the processing of the peels, while other phenolics (i.e. conjugated) could be released after hydrolysis of the cell wall linkages, thus contributing to the yield of total phenolics. Most of the conjugated phenolics in apples are esters of hydroxycinnamic acids (Vinson et al., 2001).

With regard to the extraction solvent, acetone extracted higher amounts of phenolic compounds than ethanol. In particular, the yield of phenolic compounds with ethanol was nearly 20% less than with acetone. The solubility of plant phenolics in solvents such as

249 ethanol or water is due to glycosilated forms than are more water-soluble than the related
250 aglycones. A solvent of lower polarity, such as acetone, can favour the extraction of
251 flavonoids of low-medium polarity (procyanidins) that remain otherwise bound to the alcohol-
252 insoluble matrix in apples (Guyot et al., 1998).

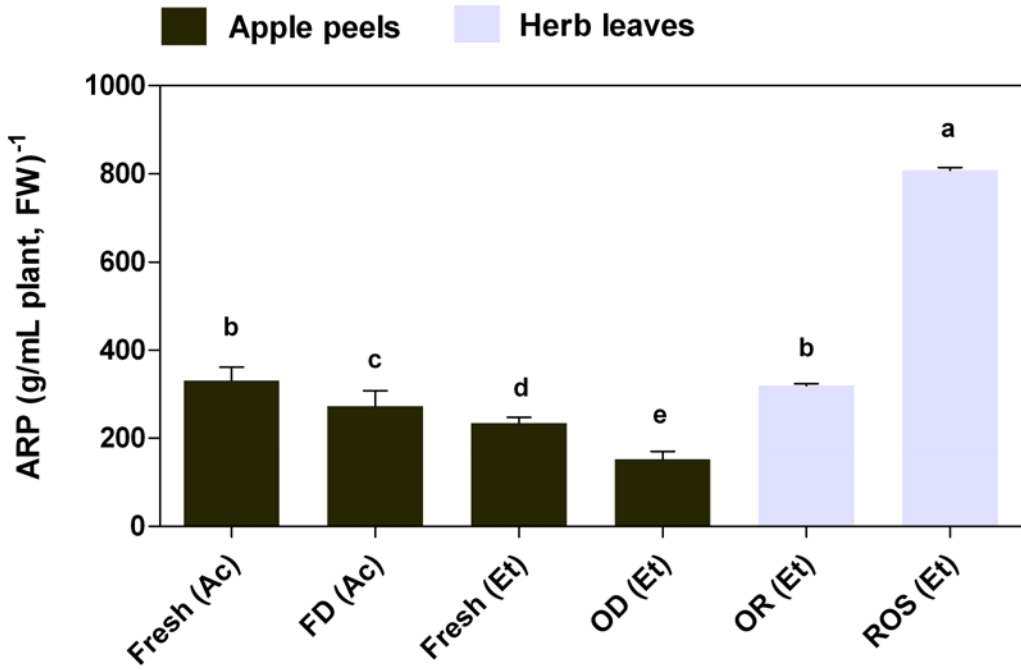
253 3.2.2 *Antioxidant capacity*

254 The ascorbic acid equivalent antioxidant capacities (AEAC) of the processed samples were
255 compared to those of fresh samples extracted under the same solvent conditions (Table 4). The
256 radical scavenging capacity (for DPPH^{*}) reduced significantly ($p < 0.05$) after the processing of
257 the peels, while the ferric reducing antioxidant power was not affected. These findings
258 suggested that the redox potential (FRAP) of the fresh sample was maintained during
259 processing because the amount of total reducing substances (including total polyphenols, TPC)
260 remained stable possibly as a result of released hydroxycinnamic acids otherwise bound in the
261 fresh tissue (Wolfe and Liu, 2003). On the contrary, the radical scavenging capacity of the
262 processed mixture lowered in comparison to fresh samples, possibly in response to the loss of
263 flavonoid compounds (TFC). In particular, it is believed that the loss of oligomeric
264 procyanidins, i.e. indicated as the most powerful antioxidants in apples (Tsao et al., 2005),
265 could influence significantly the radical scavenging capacity of the processed samples, as it is
266 known that the number and substitution patterns of hydroxyl groups on the flavonoid structure
267 is crucial for their radical scavenging capacity (Apak et al., 2007). The two antioxidant assays,
268 FRAP and DPPH, could respond differently to the antioxidant mixtures as they are based on
269 different antioxidant mechanisms (Prior et al., 2005; Foti et al., 2004). With regard to the

270 solvent, the extracts obtained with acetone showed significantly higher antioxidant capacity
271 ($p < 0.05$) than those obtained with ethanol. This was explained as due to the solubilisation of
272 higher amounts of phenolic compounds (especially flavonoids). The FRAP capacities of fresh
273 and dried peels from cv. Bramley's Seedling were in agreement with data reported for other
274 dessert apples (Khanizadeh et al., 2008). To the best of our knowledge, no AEAC values
275 measured by the DPPH assay have been reported in literature for other apple peels.

276 *3.2.3 Antiradical power*

277 The Antiradical Power (ARP) of apple peel extracts was compared to oregano and rosemary
278 leaf extracts (Figure 1).



279

280 **Figure 1** Antiradical power of apple peel and herb leaf extracts. Different superscript
281 letters denoted significant difference ($p < 0.05$) among samples. Drying: oven-
282 drying (OD); freeze-drying (FD). Extraction solvent: acetone (Ac); ethanol (Et).
283 Herbs: oregano (OR); rosemary (ROS).

284

285 The peel extracts obtained with acetone had similar antioxidant capacity than oregano leaf
286 extracts. Rosemary extract had the strongest ARP ($p < 0.05$) amongst the plant extracts
287 investigated. Fresh peels had IC_{50} values of 4.28 ± 0.23 and 3.04 ± 0.27 mg peels/mL (FW)
288 when extracted with ethanol and acetone, respectively. Dried peels had IC_{50} values of $6.51 \pm$
289 0.84 and 3.72 ± 0.48 mg peels/mL (FW), when extracted with ethanol and acetone,
290 respectively. Kondo et al. (2002) reported for the skin of dessert and cider apples IC_{50} values
291 lower than 5 mg peels/mL (in the reaction mixture, FW), that is ARP values higher than 200
292 mL/g. The ARP values for fresh peels of cv. Bramley's Seedling in this study were 234 ± 13
293 and 331 ± 30 mL/g peels (in the reaction mixture, FW), for the extracts obtained with ethanol
294 and acetone, respectively.

295 Oregano and rosemary leaf extracts had IC_{50} values of 3.13 ± 0.04 and 1.89 ± 1.12 mg
296 herb/mL (FW); these values were equivalent to 0.39 and 0.16 mg herb/mL on DW basis,
297 assuming an average moisture content of 86%, w/w, which were consistent with previous data
298 reported in literature (Koşar et al., 2005).

299 *3.2.4 Regression analysis between antioxidant capacity and phenolic content*

300 A regression analysis between the antioxidant capacity and the phenolic content of the peels
301 was carried out (Table 5). The Pearson correlation coefficients were strongly significant
302 ($p < 0.01$) between the variables. However, it was observed a higher deviation from linearity in
303 the regression values ($r\text{-square} < 0.6$) of the whole peels (fresh + dried, $n = 18$) compared to
304 dried samples ($n = 12$). This could indicate that reducing substances other than polyphenols

305 (e.g. ascorbic acid) were extracted from fresh samples and contributed to the antioxidant
 306 capacity together with phenolics. In agreement with this hypothesis, the relationship between
 307 AEAC (measured as FRAP) and the total flavonoid content (r-square<0.34) was weak; while
 308 the radical scavenging capacity was better correlated with the total flavonoid content (r-
 309 square>0.63).

310

311 **Table 5 Regression analysis between antioxidant capacity and phenolic content of**
 312 **apple peels**

<i>Antioxidant capacity (as AEAC)</i>	<i>Total phenolic content</i>		<i>Total flavonoid content</i>	
<i>Fresh+Dried</i>	<i>Corr.</i>	<i>r-square</i>	<i>Corr.</i>	<i>r-square</i>
FRAP	**	(0.66)	**	(0.34)
DPPH	**	(0.47)	**	(0.63)
<i>Dried</i>	<i>Corr.</i>	<i>r-square</i>	<i>Corr.</i>	<i>r-square</i>
FRAP	**	(0.76)	**	(0.48)
DPPH	**	(0.63)	**	(0.69)

313 ** indicated a very significant correlation between the variables (p<0.01); the linear regression fit for the
 314 correlated data was reported in brackets (R-square). AEAC: ascorbic acid equivalent antioxidant capacity; Corr.:
 315 Pearson's correlation.

316

317 In the dried samples, the contribution of phenolic compounds to the antioxidant capacity
 318 increased above 70%, particularly for flavonoids and their radical scavenging capacity, thus
 319 indicating the possible reduction of co-extracted substances, such as ascorbic acid. Results
 320 previously reported by Imeh, Khokhar (2002) for Bramley apple indicated a weak linear
 321 correlation between the antioxidant capacity (as FRAP) and the total phenolic content (r-
 322 square<0.58).

323

324 **4 CONCLUSIONS**

- 325 • The recycling value of the peels from cv. Bramley’s Seedling depended on its high levels
326 of natural antioxidants, in particular phenolic compounds that contributed significantly to
327 its antioxidant capacity.
- 328 • The recovery of target phenolic antioxidants (especially flavonoids) could be lowered by
329 the processing, i.e. cutting; drying and pulverising; however, during the processing,
330 phenolic compounds conjugated in the fresh plant matrix could be released with a
331 consequent increase of the redox potential and total phenolic content of the resulting
332 extracts.
- 333 • The drying system and the organic solvent used for the phenolic recovery affected their
334 extraction yield, consequently their antioxidant capacity. Freeze-drying protected the
335 antioxidant value better than oven-drying, while acetone favoured the solubilisation of
336 higher amounts of phenolic compounds than ethanol. The resulting extracts had equivalent
337 antioxidant power to oregano leaf extract.
- 338 • The use of oven-drying/ethanol for the phenolic recovery could lead to extracts with lower
339 antioxidant value compared to freeze-drying/acetone but with enhanced food applications.
- 340 • Further investigation on the isolation of antioxidant phenolic compounds from the peels of
341 Bramley’s Seedling apple for future food applications is desirable.

342

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346

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