

## Proximate chemical composition of orange peel and variation of phenols and antioxidant activity during convective air drying

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**Abstract:** The aim of this work is to investigate the global chemical characteristics of Tunisian Maltese orange peel and to determine the effect of air temperature (40, 60, 80°C) on phenols and antioxidant activity kinetics of orange peel. Maltese orange peel is rich in nutritional ingredients such as soluble sugars (46.241±0.015 g/100g d.b), proteins (8.120±0.120 g/100g d.b) and minerals (3.170±0.035 g/100g d.b). It contains antioxidant such as phenols (2.685±0.062 g/100 g d.b) and vitamin C (0.105±0.003 g/100 g d.b). Phenolic compounds of Maltese orange peel, expressed as g/100g orange peel powder are: neohesperidin (1.312±0.031), followed by hesperidin (0.990±0.011), naringin (0.060±0.001), nobiletin (0.109±0.001), narirutin (0.031±0.001), didymin (0.049±0.001), sinensetin (0.047±0.000), eriocitrin (0.061±0.005), 3',4',5,5',6,7,-hexamethoxyflavone (0.0070±0.0001) and tangeretin (0.019±0.001). Glycosylated flavanones (eriocitrin, narirutin, naringin, hesperidin, neohesperidin, didymin) and polymethoxylated flavones (sinensetin, 3',4',5,5',6,7,-hexamethoxyflavone, tangeretin, nobiletin) show similar behavior during air drying (at 40, 60 and 80°C): a rapid decrease of 79.86%, 81.88% and 80.46% for neohesperidin and 88.17%, 87.55% and 81.37% for hesperidin during the first hour of air drying and then amounts show little variations until the end of drying. Drying during 75 min at 80°C allows the lowest degradation of total phenols (81.72%) compared to 85.06% at 60°C (during 120 min) and 88.40% at 40°C (during 240 min). The antioxidant activity variation shows similar behavior.

**Keywords:** orange peel characterization, air drying, phenolic compounds, antioxidant activity, kinetic.

### 1. Introduction

The world citrus production is estimated at 89 million tons in 2014 (USDA 2014). Approximately 26% of citrus fruits are industrially processed into juice. The amount of world industrial waste of citrus is estimated at 15×10<sup>6</sup> tons (Marin et al. 2007). The main industrial transformation of citrus is focused on juice production. Citrus juice production results in the accumulation of huge amounts of by-products which account for about the half of the fruit weight (Bocco et al. 1998; Marin et al. 2007). The industrial by-products contain peels, seeds and pulp membrane residues. Citrus peel is an important source of essential oils, especially limonoids (Espiard 2002) which are used for the production of perfumes and other cosmetics. Limonoids have also different biological properties (antiviral, antifungal and antibacterial activities) (Ma et al. 2009). Citrus peel can be used for the production of valuable products like biogas, ethanol, or volatile flavouring compounds (Djilas et al. 2009) or used for extraction, separation and purification of bioactive molecules with great interest in the development of healthy products. Indeed, citrus peel contains many molecules with interesting properties, which can be used as natural additives in various industries such as pectin obtained from the peel by acid extraction and the whole dietary fiber obtained by mechanical processing (Djilas et al. 2009). Citrus peel represents also a rich source of natural phenolic compounds unique to citrus, especially the characteristic flavanone glycosides, mainly naringin, hesperidin, narirutin, and neohesperidin (Bocco et al. 1998). Total phenol contents of orange peel ranged from 1.13 to 7.30 g/100g d.b (Cheynier 2006; Kammoun et al. 2011), respectively. The citrus flavonoids have been



found to have health-related properties, which include antioxidant, anticancer, antiviral and anti-inflammatory activities. However, these by-products are sensitive to biochemical and microbial degradations because of their high amount of moisture (70-80%). Moreover, the phenolic compounds of citrus by-products could be submitted to enzymatic oxidation at different steps of processing. Citrus by-products stabilization is an essential step to facilitate the further uses (extractions of bioactive compounds for healthy products formulation). Dehydration at appropriate conditions, allows a decrease of moisture and water activity of the product and the inhibition of both oxidative enzymatic reaction and micro-organisms growth allowing prolonging the shelf life of the product. Convective drying process is always used for drying of agro-food and by-products. It is less expensive than freeze drying which is better appropriated to products with high added value (Lewicki 2006). The long exposition of the product to air temperature during convective drying could induce the degradation of thermo-sensitive compounds and antioxidant capacities of the product. Thus, the aims of this work were (i) to determine the proximate chemical composition of Maltease orange peel, (ii) to examine the convective air drying characteristics of “Maltease” orange peel at 40, 60, 80°C and (iii) and to investigate the effect of convective air drying temperature on the individual flavonoids and the antioxidant activity of the peel.

## 2. Material and methods

About 20 kg of fresh oranges (*Citrus sinensis*) of “Maltease” variety were collected in March 2013 from the region of Manzel Bouzalfa (Nabeul, Tunisia) at their commercial maturity. All fruits were of eating quality and without blemishes or damage. On arrival at the laboratory, the orange fruits were immediately washed by tap water and peeled. The average weight of the fruit is  $185.00 \pm 7.07$  g. The orange peel accounts for approximately 40% of the total fruit. The peels were stored at -20°C before any further treatments.

### 2.1. Chemical analysis

Moisture content was measured by the gravimetric method at 105°C up to constant weight (ISO 2004). The weighing of the orange peel samples for moisture content determination was made with a balance with a precision of 0.0001 g. Ash was determined by incineration of the sample in a muffle furnace at 550 °C for 5 h (AOAC 2006). Protein was analyzed according to the Kjeldahl method (ISO 2001). Fat content was determined by the Soxhlet method, using petroleum ether as a solvent (AOAC 1997). The determination of the soluble sugars content was achieved using the DNS colorimetric method (Miller 1959) and vitamin C was measured according to the 2,6-dichlorophenol indophenol (DCPIP) method (Tabart et al. 2010). All analytical determinations were performed in triplicate. Values of different parameters were expressed as mean value  $\pm$  standard deviation.

### 2.2. Sorption isotherms

A static gravimetric method was used to determine the sorption isotherms of orange peel at 40, 60 and 80°C. Different saturated salt solutions were used. Each solution was placed into a separate glass jar, to which the samples were added and then sealed. Triplicate fresh orange peel samples of  $0.500 \pm 0.001$  g were placed in the hermetically sealed jars which were then placed in a controlled oven temperature. The weight of samples was determined until weight stabilization. It was thus assumed that moisture equilibrium was reached. The equilibrium moisture contents were measured by drying the samples at 105°C for 24h (AOAC 1997).

### 2.3. Orange peel dehydration

The initial moisture content of frozen orange peel was  $79.80 \pm 0.015\%$ . Convective air drying experiments were carried out at pilot scale by placing a thin layer of Maltease orange frozen peel “Maltease” variety in a basket placed inside a cross-flow tunnel dryer, at the following temperatures: 40, 60 and 80°C, at an air flow rate of 1.2 m/s and at ambient relative air humidity varying from 3.5 to 10.6 %. The dryer was composed of a wind tunnel providing an air flow of 10-100 m<sup>3</sup>/h, a 40  $\Omega$  heating resistance and a tunnel allowing fluidized or fixed bed drying. For all experiments, moisture loss was recorded at different drying times by weighting the orange peel with a balance with a precision of 0.1g. For each drying experiment, peel samples were removed from the dryer at different times for moisture, phenols determination and antioxidant activity measurements. The drying was

continued until the weight of the samples reduced to a level corresponding to a constant weight and to a moisture content inferior to 0.10 kg water/kg db. Freeze drying was used as the control drying process. For this, another sample of frozen Maltease orange peel was dried by using a freeze dryer (CHRIST Alpha 1-2 LD, France) at 50°C and 0,001 mbar during 72h.

The variation of individual phenolic compounds and antioxidant activity of orange peel during convective air drying was expressed as reduced values and were determined as follows:

$C/C_0$ : C: phenol compound content determined in dried peel at 40, 60 or 80°C;  $C_0$ : Phenol compound content determined in freeze dried peel (control).

$A/A_0$ : A: antioxidant activity of the ethanoic extract determined in dried peel 40, 60 or 80°C;  $A_0$ : antioxidant activity determined in freeze dried peel (control).

#### 2.4. Conventional solvent extraction

Dried orange peel samples were ground using a coffee grinder (Moulinex®, France) and sifted through a mesh screen to achieve a standard particles size of ~ 0.315 mm. The orange peel powders were placed in vacuum packaging bags and stored in a freezer maintained at -18°C before further extractions. Five grams of *citrus sinensis* peel powder were extracted with 50 ml of 80% ethanol. The mixture was shaken at 200 rpm in darkness by using a mechanical stirrer for 30 min at 35°C. The crude extract was centrifuged at 8000g for 10 min and the supernatant was filtered through a 0.2 µm solvent filter. The residue was further extracted two times with 50 ml of the same solvent under the same extraction conditions. Combination of the three extracts were collected and stored at 4°C. Each measurement was performed three times.

#### 2.5. Analysis of phenolic by HPLC

Identification of phenolic compounds of Maltease orange peel is done in two steps: identification by mass spectrometry and confirmation by HPLC analysis with the injection of standards. The quantitative analysis was performed by using an HPLC analytical system (Elite LaChrom, VWR-Hitachi, France) consisting of a Spectra System P4000 pump, a Spectra System UV 6000LP diode array detector, a Spectra System SCM 1000 degasser and a Spectra System AS3000 auto-sampler controlled by software (Thermo Chromquest). After filtration on Millipore paper (0.22 µm), 20 µl of ethanolic extract was injected on reverse-phase  $C_{18}$  column (150×4.6 mm, 5 µm particle size, Apollo, Grace, Belgium). The mobile phase consisted of solvent A, water-acetic acid (2%) and solvent B, methanol-acetic acid (2%). A gradient program was carried: out as follows: 5 min, 10% B ; 78 min, 100% B ; 88 min, 100% B ; 90 min, 10% B ; 100 min, 10% B. The flow rate was 1 ml/min, and the temperature of the column oven was 40°C. The limits of detection of the HPLC used for the flavonoid analysis are 9000 u.a. for the detection at 290 nm and 50 u.a. for the detection at 340 nm. The limits of quantification were calculated according to each standard curve. The standards eriocitrin, naringin, narirutin, neohesperidin, didymin, sinensetin, tangeretin, nobiletin and 3', 4', 5, 5', 6, 7,- hexamethoxyflavone were prepared at a stock concentration of 250 mg/L. For hesperidin, the concentration was 20 mg/L because of its low solubility. Calibration standard samples were prepared by appropriate dilutions with a mixture of ethanol/DMSO from the stock solutions and filtered on Millipore paper (0.22 µm) before use. Calibration curves obtained showed determination coefficients superior to 0.98.

#### 2.6. Determination of antioxidant activity by ABTS assay

The free radical scavenging activities of orange peel extracts were determined by ABTS radical cation decolorization assay (Re et al. 1999) with minor modifications. A stable stock solution of (ABTS•+) was produced by reacting a 7 mmol/L aqueous solution of ABTS with 2.45 mmol/L potassium persulfate. After the addition of 220 µl of diluted (ABTS•+) solution to 80 µl of orange peel extract or standard Trolox in ethanol, the absorbance reading was taken at 30°C, exactly 1 min after initial mixing ( $OD_0$ ) and again at 15 min ( $OD_t$ ). The inhibition percentage of absorbance at 734 nm, using a spectrofluorometer (SAFAS flx Xenius, Monaco) was calculated between  $OD_0$  and  $OD_t$ , according to the following **equation 1** with  $OD_0$  as initial optical density and  $OD_t$  as final optical density. Appropriate solvent blanks were run in each assay.

$$\text{Percentage of inhibition} = \frac{(OD_0 - OD_t)}{OD_0} \times 100 \quad (\text{Eq 1})$$

Then, TEAC was determined according **equation 2**.

$$TEAC = \frac{a_s}{a_T} \quad (Eq 2)$$

$a_s$ : line slope for sample of percentage of inhibition (%) plotted vs. concentration ( $\mu$ M).  $a_T$ : line slope for Trolox reference of percentage of inhibition (%) plotted vs. concentration ( $\mu$ M).

### 3. Results and discussion

#### 3.1. Chemical composition

Table 1 illustrates the chemical composition (moisture, soluble sugars, proteins, ash, fat), the contents of antioxidants (total phenols, vitamin C) and the pH of Maltease orange peel. Table 1 shows that orange peel is rich in water ( $3.169 \pm 0.123$  g water/g dry basis, *i.e.*  $76.015 \pm 0.054\%$  wet basis), in nutritional ingredients such as soluble sugars ( $46.241 \pm 0.015$  g/100g d.b), proteins ( $8.120 \pm 0.120$  g/100g d.b) and minerals ( $3.170 \pm 0.035$  g/100g d.b). However, this by-product contains a low fat content ( $0.800 \pm 0.030$  g/100 g d.b). Orange peel is also rich in antioxidant such as vitamin C ( $0.105 \pm 0.003$  g/100 g d.b), and total flavonoids ( $2.685 \pm 0.062$  g/100 g d.b). By comparing the chemical composition of orange peel Maltease variety with that of other citrus varieties (orange, lemon, tangerine, and grapefruit), we can conclude that citrus peel have these common characteristics (Table 1):

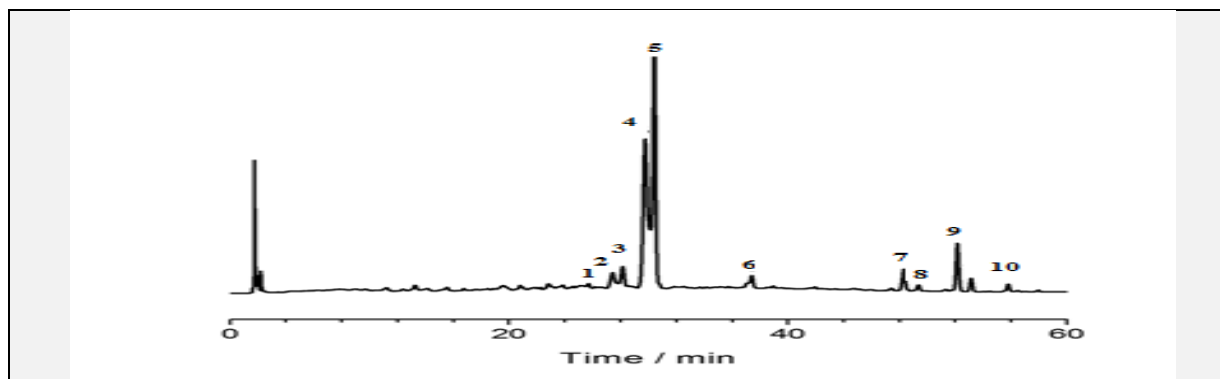
- (i) a very high level of water  $\geq 75\%$  making this by-product highly perishable and requiring immediate use or stabilization to prevent fermentation and mold growth,
- (ii) a total solid extract mainly constituted of soluble sugars (6.52 to 47.81 g/100 g d.b), proteins (1.79 to 9.06 g/100 g d.b) and minerals (2.52 to 10.03 g/100 g d.b). The total citrus solid extract is characterized by a low fat content (0.48 to 4.00 g/100 g d.b) (Kammoun et al. 2011; Ghanem et al. 2012; Marin et al. 2007),
- (iii) a high antioxidant potential represented by vitamin C (0.109 to 1.150 g/100 g d.b) and phenols (0.67 to 22.3 g/100 d.b) (Kammoun et al. 2011; Ghanem et al. 2012; Lagha-Bernamrouche et al. 2013; Chen et al. 2011; Cheynier et al. 2006; Ghasemi et al. 2009; Barros et al. 2012). The difference in the levels of nutritional and antioxidant compounds in citrus varieties or within the same variety can be attributed to pedoclimatic factors (soil type, sun exposure and precipitation), genetic factors (variety), agricultural factors (organic farming, tree fruit production, the state of maturation, growing area, fertilization, irrigation) (Causse et al. 2007) and used analytical methods (M'hiri et al. 2014).

Component	Orange Maltease <i>This work</i>	Orange Maltease <i>Kammoun et al. (2011)</i>	Others citrus varieties*
<b>Moisture</b> <sup>(a, b)</sup>	$3.169 \pm 0.123$ $76.015 \pm 0.054$	$2.970 \pm 0.083$ $74.804 \pm 0.524$	3.01-3.79
<b>Soluble sugars</b> <sup>(c)</sup>	$46.241 \pm 0.015$	$46.241 \pm 0.015$	6,52-47.81
<b>Proteins</b> <sup>(c)</sup>	$8.120 \pm 0.120$	$8.015 \pm 0.374$	1.79-9.06
<b>Ash</b> <sup>(c)</sup>	$3.170 \pm 0.035$	$3.313 \pm 0.024$	2.52-10.03
<b>Fat</b> <sup>(c)</sup>	$0.800 \pm 0.030$	$0.955 \pm 0.033$	0.48-4.00
<b>Total flavonoids</b> <sup>(c)</sup>	$2.685 \pm 0.062$	$1.13 \pm 0.04$	0.67-22.32
<b>Vitamin C</b> <sup>(c)</sup>	$0.105 \pm 0.003$	-	0.109-1.150
<b>pH</b>	$5.670 \pm 0.010$	$5.257 \pm 0.006$	-
<b>Antioxidant activity</b> <sup>(d)</sup>	$0.014 \pm 0.000$	-	-

<sup>(a)</sup> g water/g d.b ; <sup>(b)</sup> % (wet basis) ; <sup>(c)</sup> g/100g d.b ; <sup>(d)</sup> g TEAC/100g d.b. \*Kammoun et al. 2011; Ghanem et al. 2012 ; Marin et al. 2007; Lagha-Bernamrouche et al. 2013 ; Chen et al. 2011 ; Cheynier et al. 2006 ; Ghasemi et al. 2009 ; Barros et al. 2012.

#### 3.2. Phenolic composition

The quantitative and qualitative determination of phenols of Maltease orange peel was reported for the first time by M'hiri et al. (2015). The phenolic profile of Maltease orange peel was determined by using high performance liquid chromatography coupled with mass spectrometry (HPLC-MS). The chromatogram of the ethanoic extract of orange peel Maltease variety is shown in Figure 1. Eleven peaks were detected; one single compound was identified by MS but not confirmed by HPLC. Considering its molecular weight, it has been assumed to be the methoxynobiletin (3, 5, 6, 7, 8, 3', 4'-heptamethoxyflavone). Table 2 summarizes the results obtained by HPLC, LC-MS and UV  $\lambda_{max}$  of the phenolic compounds identified in Maltease orange peel.



**Figure 1.** Chromatogram of ethanoic extract of orange peel Maltease variety obtained by HPLC-DAD-MS at 279 nm. Conventional solvent extraction: m/v: 5 g/50 ml, 30 min, 35°C, 80% ethanol, mechanical agitation in the dark and three successive extractions. (1) Eriocitrin; (2) Narirutin; (3) naringin; (4) Hesperidin; (5) Neohesperidin; (6) Didymin; (7) Sinensetin, (8) 3', 4', 5,5', 6,7-Hexamethoxyflavone; (9) nobiletin; (10) tangeretin.

All phenolic compounds identified in ethanoic extract of Maltease orange peel are flavonoids: six glycosylated flavanone (neohesperidin, hesperidin, narirutin, naringin, didymin, eriocitrin) and four polymethoxylated flavones: (sinensetin, tangeretin, nobiletin, hexamethoxyflavone). Except narirutin and eriocitrin, similar composition was reported by Anagnostopoulou et al. (2005) in Greek Navel sweet orange peel. However, this variety contains also pentamethoxyflavone.

**Table 2.**  $R_t$ , pseudomolecular ions, adduct ions with  $Na^+$ , and  $UV_{max}$  of orange peel phenolic compounds identified by HPLC-DAD-MS. Conventional solvent extraction: m/v:5g:50ml, 30 min, 35°C, ethanol 80%, mechanical agitation at darkness and 3 extraction cycles.

Compound	$R_t$ (min)	$[M+H]^+$ (m/z)	$[M+Na]^+$ (m/z)	UV $\lambda_{max}$ (nm)	Identification
1	22.80	597	619	284, 327	Eriocitrin
2	31.85	581	603	284, 329	Narirutin
3	31.97	581	603	280, 328	Naringin
4	33.10	611	633	284, 328	Hesperidin
5	33.95	611	633	285,327	Neohesperidin
6	40.77	595	617	226, 284, 332	Didymin
7	51.58	373	395	240, 264, 328	Sinensetin
8	52.37	403	425	237, 268,320	3',4', 5,5'6,7, Hexamethoxyflavone
9	55.29	402	425	249, 271, 334	Nobiletin
10	58.54	372	395	271, 324	Tangeretin

Table 3 shows the contents of the identified flavonoids. Flavanones correspond to 93.22% of total phenols and include: eriocitrin, narirutin, naringin, hesperidin, neohesperidin, didymin. Polymethoxylated flavones present 6.78% of total phenols and include: sinensetin, 3', 4', 5, 5', 6, 7-hexamethoxyflavone, tangeretin and nobiletin.

**Table 3.** Phenolic composition of Maltease orange peel.

Phenolic compound	Orange peel* Maltease (This work) (g/100g orange peel powder )	Orange peel Maltease (This work) (% total phenols)	Citrus peel <sup>a</sup> Literature (g/ 100g d.b)
Eriocitrin	0.061±0.005	2.27	-
Narirutin	0.031±0.001	1.15	0.003-2.65
Naringin	0.060±0.001	2.23	0.008-1.44
Hesperidin	0.990±0.011	36.87	0.0002-8.09
Neohesperidin	1.312±0.031	48.88	0.005-0.79
Didymin	0.049±0.001	1.82	-
Sinensetin	0.047±0.000	1.75	0.008-0.029
3',4', 5,5'6,7, hexamethoxyflavone	0.0070±0.00001	0.26	-
Nobiletin	0.109±0.001	4.06	0.020-1.405
Tangeretin	0.019±0.001	0.71	0.016-0.799

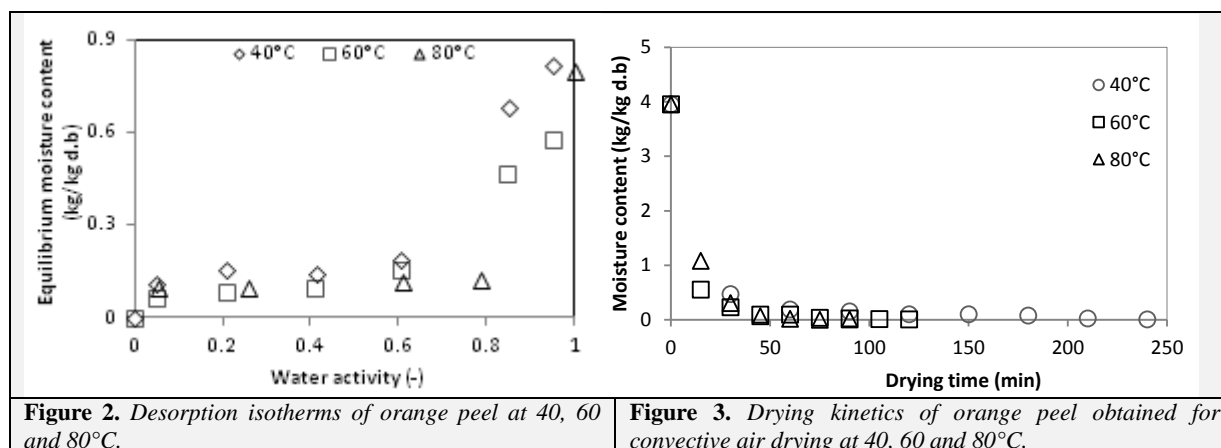
<sup>a</sup>Freeze dried orange peel; Cheymier et al. 2006; Wang et al. 2008; Bocco et al. 1998; Russo et al. 2014; Goulas et al. 2012; Cheigh et al. 2012; Sawalha et al. 2009.

The comparison of phenolic profile of Maltease orange peel with that of other citrus peel variety shows that the amounts of phenolic compounds vary according to citrus variety. For example, the most abundant compounds in orange peel, regardless of the variety are: hesperidin (0.066 to 66.095 mg/g d.b) followed by narirutin (0.025 to 26.5 mg/g d.b). Whereas in the bitter orange peel, the major phenolic compounds are: naringin (1.1 to 5.10 mg/g d.b) and neohesperidin (0.66 to 7.9 mg/g d.b). The neoeriocitrin is abundant in lemon and lime (0.5 to 6.12 mg/g d.b) (Bocco et al.1998; Cheynier et al. 2006; Sawalha et al. 2009).

Comparing the phenolic profile of Maltease orange peel with the other varieties of citrus fruits, it can be concluded that flavanones and polymethoxyflavones are the characteristics flavonoids of citrus peel with specific quantitative and qualitative variations of major compounds according to citrus variety. According to the literature, citrus peel may also contain flavonols and hydroxycinnamic acids which are detected in traces.

### 3.3. Desorption isotherms and evolution of moisture content of orange peel during drying

Desorption isotherm represents the relation between the water activity in the product and its moisture content. It is of great importance in the design of food dehydration processes particularly in the determination of the final moisture content. Desorption isotherms of orange peel at 40, 60 and 80°C were presented in Figure 2.



Desorption curves permitted to determine, for a determined water activity, the final moisture contents reached at different drying temperatures in order to ensure physicochemical and microbial stability of the by-product during processing and storage. Effectively, to guarantee the product quality, it is recommended to reach and maintain a water activity inferior to 0.6 as the upper limit during storage to avoid microbial growth (Cordeiro et al. 2006). According to Figure 2, in order to reach a water activity inferior to 0.6, Citrus peel should be dried until moisture content equal or inferior to 0.1 kg/kg d.b.

The variation of moisture contents versus drying time of the orange peel at 40, 60 and 80°C are shown in Figure 3. The increase of air temperature led to a significant decrease in the drying time: 240 min at 40°C; 120 min at 60°C and 75 min at 80°C. The moisture contents of the product obtained at different drying times were used for the expression of the phenolic compounds contents and antioxidant activities of dried peel in dry basis at different drying times.

### 3.5. Degradation kinetics of flavonoids and antioxidant activity of air dried orange peel

Neohesperidin and hesperidin are the major phenolic compounds of the freeze dried orange peel (1.312±0.031; 0.990±0.011 g/100g orange peel powder, respectively). The amounts of the other phenolic compounds determined in freeze dried peel vary from 0.0070± 0.0001 g/100 orange peel powder (3',4', 5,5',6,7, hexamethoxyflavone) to 0.109±0.001 g/100 orange peel powder (nobiletin). Figure 4 shows the variation of reduced total phenol content of orange peel during air drying at 40, 60 and 80°C. The increase of temperature accelerates the rate of dehydration and phenol degradation but drying at high temperatures (60 and 80°C) allows better phenols retention at the end of drying process. It can be noticed that the most changes: moisture removal and phenols degradation occur at the first

hour of drying and are accelerated by increasing air temperature. Total phenol contents of the peel decrease rapidly during the first hour of drying and then stabilize at different levels until the end of drying: 88.40, 85.06, 81.72% at 40, 60, 80°C, respectively. The change rate of individual flavonoids of dried orange peel during drying at 80, 60 and 40°C was dependent on the type of the flavonoid, on the applied air temperature and on reached moisture content of the product.

Figure 5 shows the evolution of the total antioxidant activity of orange peel during drying. Antioxidant activity decreased with the drying time (82.86; 77.14; 76.43 % at 40, 60, 80°C, respectively). Drying at higher temperature (60 and 80°C) permits the lower degradation of the antioxidant activity of orange compared to antioxidant activity at 40°C. The kinetics of the total and major individual flavonoids are in concordance with the variation of orange peel antioxidant activity during air drying at the investigated temperatures

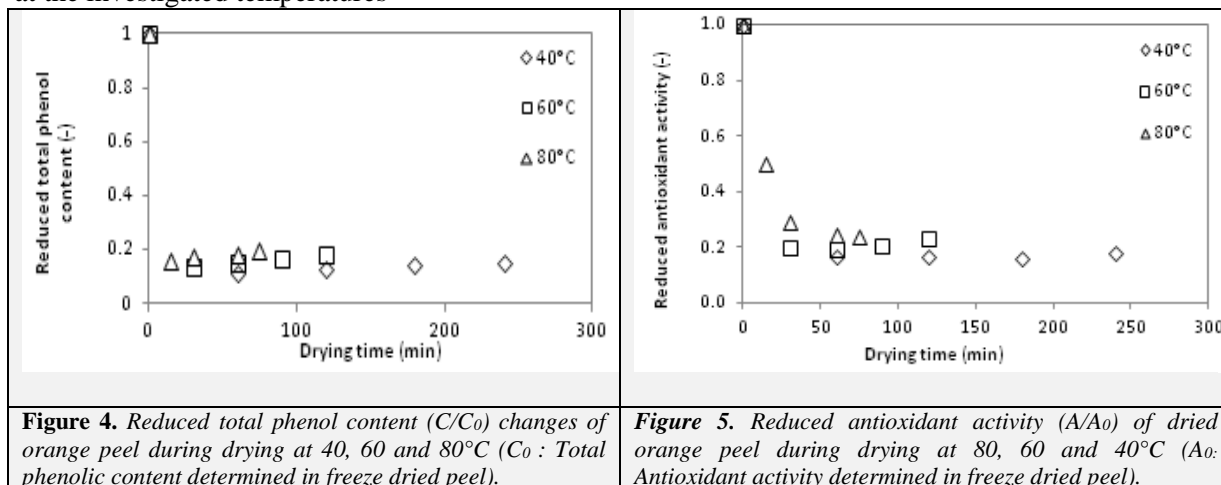
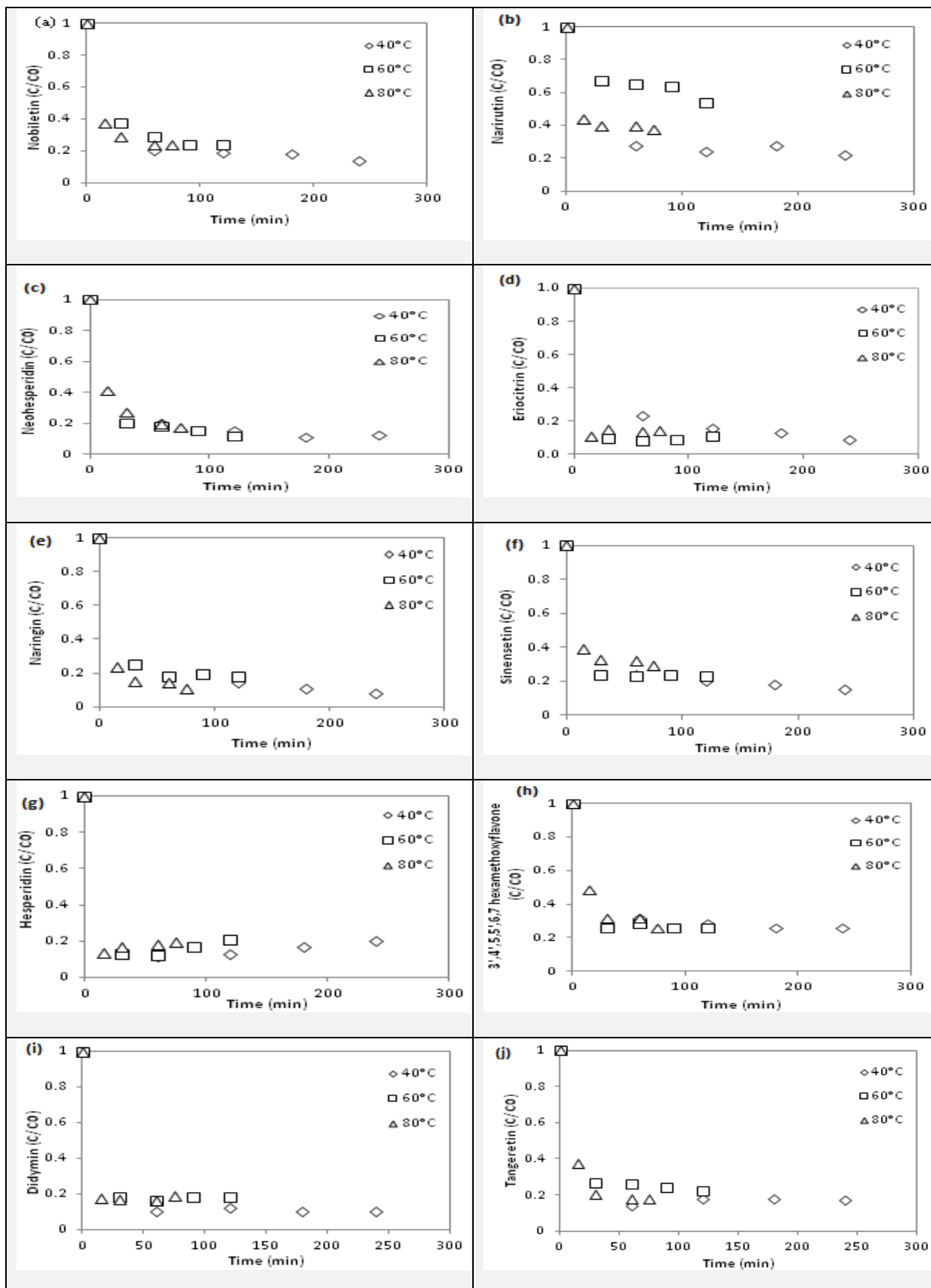


Figure 6 shows that neohesperidin and hesperidin are better retained at the end of drying at 80°C. Eriocitrin, didymin, nobiletin, sinensetin, naringin, narirutin, 3',4', 5,5',6,7, hexamethoxyflavone and tangeretin contents changes show the same trend. It can be concluded that drying during 75 min at 80°C allows obtaining the highest content of phenolic compounds followed by drying during 120 min at 60°C and 40°C during 240 min.

The enzymatic oxidation by polyphenoloxidase was reported by Devic et al. (2010) and Djendoubi et al. (2012) as the main mechanism of phenol degradation during convective drying. Li et al. (2006) explained the decrease of phenols during drying by the fact that long exposition to drying and high temperature levels may damage some of the phenolic compounds. Garau et al. (2007) studied the effect of air drying temperature (from 30°C to 90°C) on the antioxidant activity of citrus by-products. The authors reported that drying at higher temperatures (80 and 90°C) or at temperatures which implied longer drying times (30 and 40°C) promoted a decrease of the antioxidant capacity. They concluded that the most appropriate drying temperature allowing preservation of the antioxidant capacity of citrus by-products could be around 60°C, suggesting that antioxidant compounds from peel samples have a higher resistance to heat degradation.

Kuljarachanan et al. (2009) reported also that drying of lime residues at 60°C could retain the highest antioxidant activity. Chen et al. (2011) investigated the effect of different drying temperatures (50, 60, 70, 80, 90 and 100°C) on changes in the flavonoids, phenolic acids and antioxidant activity of *Citrus sinensis* peel. The authors noted that the highest total phenolic content was in the peel dried at 100°C ( $65.72 \pm 3.42$  compared to  $39.45 \pm 1.00$  GAE mg/g d.b for fresh peel). Ho et al. (2008) investigated the effect of heating treatment conditions for enhancing the anti-inflammatory activity of *Citrus reticulata* peel. They indicated that the content of total flavonoids increased up significantly with heat treatment from 7.62 mg catechin equivalents/g extract for the unheated control to 9.07 mg catechin equivalents/g extract by heating at 100°C for 180 min. The content of nobiletin and tangeretin obtained in the extract of citrus peel, heated at 180 min increased by 22.4% and 13.8%, respectively. The authors explained the increase by the fact that heat treatment can release some phenolic compounds from covalently bound form to extractable form.



**Figure 6.** Reduced contents (C/C<sub>0</sub>) of nobiletin (a), narirutin (b), neohesperidin (c) eriocitrin (d), naringin (e), sinensetin (f), hesperidin (g), 3', 4',5', 5',6',7,-hexamethoxyflavone (h), didymin (i) and tangeretin (j) determined during drying at 40, 60 and 80°C; C: Phenol compound content determined in air dried peel; C<sub>0</sub>: Phenol compound content determined in freeze dried peel.



#### 4. Conclusion

Citrus peel is rich in nutritional ingredients such as soluble sugars ( $46.241 \pm 0.015$  g/100g d.b), proteins ( $8.120 \pm 0.120$  g/100g d.b) and minerals ( $3.170 \pm 0.035$  g/100g d.b). It contains antioxidant such as flavonoids ( $2.685 \pm 0.062$  g/100 g d.b) and vitamin C ( $0.105 \pm 0.003$  g/100 g d.b). The flavonoids compounds determined in freeze dried citrus peel, expressed as g/100g orange peel powder are: neohesperidin ( $1.312 \pm 0.031$ ), followed by hesperidin ( $0.990 \pm 0.011$ ), naringin ( $0.060 \pm 0.001$ ), nobiletin ( $0.109 \pm 0.001$ ), narirutin ( $0.031 \pm 0.001$ ), didymin ( $0.049 \pm 0.001$ ), sinensetin ( $0.047 \pm 0.001$ ), eriocitrin ( $0.061 \pm 0.005$ ), 3', 4', 5, 5', 6, 7, -hexamethoxyflavone ( $0.0070 \pm 0.0001$ ) and tangeretin ( $0.019 \pm 0.001$ ). The effect of convective air drying temperature (40, 60 and 80°C) on flavonoids and antioxidant activity of orange peel by taking into account freeze drying as a control process was investigated. Individual flavonoid compounds kinetics of orange peel is dependent on the type of flavonoid and on moisture content and drying temperature. The kinetics of total and the individual compounds show a rapid degradation during the first hour of drying. Drying during 75 min at 80°C allows obtaining the highest content of major individual flavonoids and antioxidant activity of orange peel compared to drying at 60°C during 120 min and at 40°C during 240 min.

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