Agronomy Research **14**(S2), 1442–1450, 2016

Changes in the total phenol content in the industrial potato peel wastes during the storage

I. Shepelev*, R. Galoburda and T. Rakcejeva

Latvia University of Agriculture, Faculty of Food Technology, St. Liela 2, LV-3001 Jelgava, Latvia
*Correspondence: igor_shepelev@inbox.lv

Abstract. As a zero value by-product from the economic point of view, potato (*Solanum tuberosum* L.) peel is a good source of phenols. As a manufacturing waste, potato peels are stored at the uncontrolled conditions and are exposed to the fermentative, oxidative, and microbial degradation. The aim of the present study was to determine the phenol degradation dynamics in the stored peels so the maximum storage time could be defined to achieve the efficient phenol extraction. Three different types of samples were prepared by abrasion peeling method and stored at room temperature, in open air, up to six days. Phenol extracts were obtained using ethanol-based solvent. Total phenol content was expressed as a gallic acid equivalent; antiradical activity was measured using the 2,2-diphenyl-1-picrylhydrazylradical. Results revealed that total phenols during the storage are more stable in the larger peel samples that can be stored up to two days without significant changes in the total polyphenol content and antiradical activity. Finely shredded peel demonstrated significant decrease in the total phenol amount and in the antiradical activity already on the second day of the storage. This fact indicated that in the finely shredded peel samples phenols are easily accessible to the oxidative and fermentative processes. It is possible, that after peeling there were big amounts of chlorogenic acid in the samples. When total amount of polyphenols decreased, chlorogenic acid degraded and caffeic acid was released in sufficient amount to hold antiradical activity of the extract on the high level.

Key words: antiradical activity, potato peel utilization, phenols.

INTRODUCTION

Worldwide, potato (*Solanum tuberosum* L.) production is growing annually and it reached 376.5 million tons in 2013 (FOASTAT, 2013). It is one of the most important agricultural crops for human consumption after wheat (*Triticum* L.), rice (*Oryza* L.), and maize (*Zea mays subsp. mays* L.), due to its low cost, low fat and high carbohydrate contents, valuable proteins, fibres, and another compounds. In the developed countries, the biggest part of the harvest is processed and potato waste (PW) amounts can reach up to 40% of the initial product amount depending on the quality of the raw material and processing technology. Because of the high availability of the specialized animal feed and the high water content in the PW, cattle breeders lose their interest in the PW application that results in the utilization problems. At the same time, Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 require minimization of the produced waste amounts and several goals are established by year 2020 (Directive 2008/98/EC, 2008). Biogas production is an alternative way of the PW

recycling, but it leads to a loss of various valuable compounds that can be extracted and applied in the food production.

There are various types of PW depending on the potato processing method (Ahokas et al., 2014) and the most common is potato peels (PP). PP contain high amount of water (83.29 g 100 g^{-1}), is a good source of carbohydrates (12.44 g 100 g^{-1}), also contain proteins (2.57 g 100 g^{-1}), lipids (0.10 g 100 g^{-1}), and dietary fibres (2.5 g 100 g^{-1}) (USDA, 2015). In addition, PP is a good source of phenolic compounds (up to 977 mg 100 g^{-1} on a dry weight basis in gallic acid equivalents (GAE)) (Makris et al., 2007), which content varies greatly depending on the potato cultivars (Albishi et al., 2013; Murniece et al., 2014).

Many scientific articles are discussing extraction of phenol compounds form the PP (Al-Weshahy & Rao, 2009; Schieber & Saldaña, 2009; Singh & Saldaña, 2011; Luthria, 2012; Wijngaard et al., 2012; Albishi et al., 2013; Cardoso et al., 2013; Amado et al., 2014; Sánchez Maldonado et al., 2014; Sabeena Farvin et al., 2012), possible application of the peel extract in the food production (Mansour & Khalil, 2000; Zia-Ur-Rehman et al., 2004; Koduvayur Habeebullah et al., 2010; Nayak et al., 2011; Pasqualone et al., 2013; Shah et al., 2014), and its effect on the health (Singh & Rajini, 2004; Singh et al., 2008; Singh & Rajini, 2008). In most studies, peel samples were used for the active compound extraction right after peeling. However, it is very interesting to investigate the possibility of industrial potato processing waste accumulation for further processing. Therefore, the aim of the present study was to determine the phenol degradation dynamics in the stored potato peels for establishing the maximum storage time to achieve the efficient phenol extraction.

MATERIALS AND METHODS

Chemicals and reagents

Agricultural origin ethanol (96.6%) was purchased from Stumbras (Kaunas, Lithuania), Folin-Ciocalteu phenol reagent, Na_2CO_3 and 2,2-diphenyl-1-picrylhydrazyl radical ($DPPH^{\bullet}$, 95%) from Merck (Darmstadt, Germany).

Sample preparation

Potato tuber samples (*Solanum tuberosum* cv Magdalena, pedigree 82-28.9/15876.41) were received from the State Priekuli Plant Breeding Institute. Cultivar has yellow flesh and red peel.

Based on the previous study of the peel samples from the potato processing facilities in Latvia, three types of samples were prepared using the abrasion peeling method: a) big peel flakes (3–5 cm), b) small peel particles (3–5 mm), and c) finely shredded peel. Samples were stored in the open plastic containers from 1 to 6 days at 20 ± 3 °C in open air without additional aeration. After collection, samples were freeze-dried in the laboratory dryer FT33 (Armfield, UK) up to approximately 5% moisture content and ground in the laboratory mill KN 195 Knifetec (Foss, Denmark) till the fine PP powder was received. Remaining moisture content was determined by gravimetric method by drying the acquired PP powder at 105 °C to a constant weight. PP powder was immediately used for the phenol extraction without any additional storage. The whole experiment was repeated in three consecutive batches.

Extraction

Extraction was performed according to the method described by Mane et al. (2015) with some modifications. 20 mL of the ethanol-water solvent (4:1; v/v) was mixed with 2 g of the PP powder. Mixture was placed in the laboratory ultrasonic bath YJ5120–1 (Zhengzhou Henan, China) for 15 minutes at 33 ± 1 °C. Then mixture was centrifuged for 15 min at 3,000 s^{-1} and filtered. Extraction was repeated three times. Combined supernatants were used for the determination of the total phenol content and antioxidant activity.

Determination of the total phenol content

Jung et al. (2011) method with slight modifications was applied. Briefly, 200 µL of the extract solution was mixed with 1 mL of distilled water and 100 µL of Folin-Ciocalteu phenol reagent (preciously diluted with distilled water 1:1, v/v). After 5 min, 2 mL of the 10% sodium carbonate solution was added and mixture was allowed to stand at room temperature for 60 min, and then centrifuged at 3,500 s^{-1} for 10 min. The absorbance was measured at 725 nm by laboratory spectrophotometer Jenway 6300 (Stone, United Kingdom). Results were recalculated per dry matter and expressed as GAE.

Determination of the free radical scavenging activity

2,2-diphenyl-1-picrylhydrazyl radical (DPPH$^{\bullet}$) was used for *in vitro* determination of free radical scavenging activity (Yu et al., 2003). 0.5 mL of extract was mixed with 0.004% DPPH$^{\bullet}$ ethanol solution. Mixture was allowed to stand for 30 min in the dark at room temperature. The absorbance was measured at 517 nm by laboratory spectrophotometer Jenway 6300 (Stone, United Kingdom). The percentage of remaining DPPH$^{\bullet}$ was calculated as follows:

$$(\%) = (1 - \frac{A_{sample}}{A_{control}}) \times 100 \quad (1)$$

where: $A_{control}$ – absorbance of the control sample; A_{sample} – absorbance of the analysed sample.

Statistical methods

One-way ANOVA ($P \leq 0.05$) and Tukey's test were applied for the statistical analysis of the effect of the storage time on the total phenol content and effect of the storage time on the free radical scavenging activity of the potato peel extracts.

RESULTS AND DISCUSSION

Results show that during the storage at uncontrolled conditions phenols are more stable in the larger peel samples (large flakes and small particles) than in the finely shredded peel samples.

During the first minutes after peeling, peel samples showed signs of the browning, which indicated a presence of the fermentative reactions. Vamos-Vigyazo (1981) had reported that polyphenol oxidase (PPO) in potatoes catalyzes the conversion of monophenols to *o*-diphenols and *o*-dihydroxyphenols to *o*-quinones. After that, quinine products can polymerize and react with amino acid groups of cellular proteins that will

lead to brown pigment appearing. In addition, Thygesen et al. (1995) showed that the highest activity of the PPO is in the subepidermal or outer cortex layer, in distance of 1.5–2.0 mm from the skin. Exactly the layer that is taken off by abrasion peeling methods that are applied in the Latvian potato processing facilities.

Strong obnoxious smell appeared after the first day of storage in the finely shredded peel samples, that is a sign of putrefaction and microbial degradation. Meanwhile, cell condition could be a reason that larger peel samples had no signs of the microbial spoilage during the tested storage time.

Fig. 1 shows the effect of the storage time on the total phenol content in the samples. No significant difference was observed between large peel flakes and small peel particles. Total phenol amount was stable during the first two days of storage and showed a significant decline on the third, by 40% comparing to the average of the previous days. Meanwhile, finely shredded peal show significant decrease already on the second day of the storage, by 66%. Difference in the peel sample physical conditions and total phenol content indicate that in the phenols in finely shredded peel samples are more easily exposed to the fermentative and microbial degradation, while in the larger peel samples the whole structure of the cell can express a protective effect.

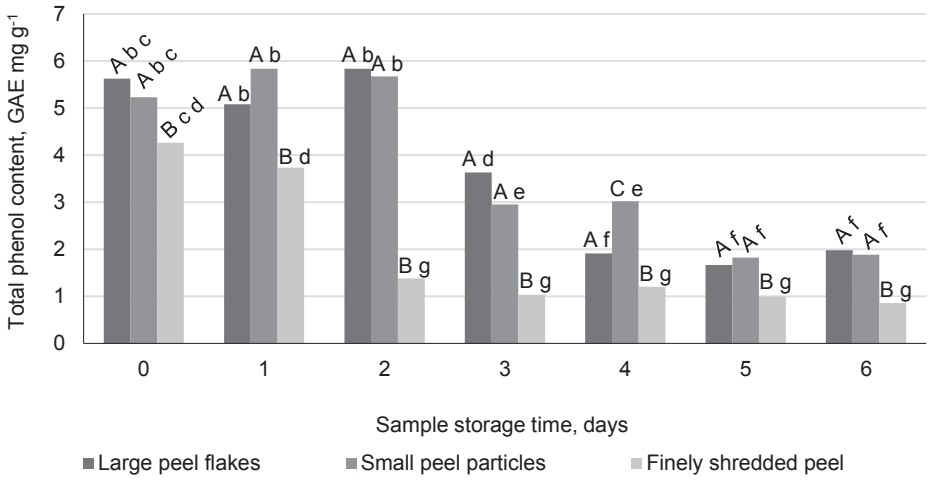

Figure 1. Effect of the storage time at uncontrolled conditions on the total phenol content in the potato peel samples. The data is presented as a mean (n = 9). Similar lowercase letters indicate no significant difference among samples ($P \leq 0.05$); similar uppercase letters indicate no significant difference among peel types within each day separately ($P \leq 0.05$).

Fig. 2 shows the effect of the storage time at uncontrolled conditions on the free radical scavenging activity of the potato peel extracts. After the first day of storage all three types of PP samples showed no significant changes in the antiradical activity, but on the second day finely shredded peel had lost 97% of its antiradical activity while activity of the larger peel samples stayed at the previous level. Only on the third day of storage, larger peel samples started to show the first significant decline in its antiradical activity.

It can be observed (Fig. 3) that correlation between total phenol content and antiradical scavenging activity is not linear. It is well known that chlorogenic acid and caffeic acid are two of the main phenols in potatoes (*Solanum tuberosum* L.) and both act as antioxidants (Mattila & Hellström, 2007; Al-Weshahy & Rao, 2009; Koduvayur Habeebullah et al., 2010; Singh & Saldaña, 2011; Wu et al., 2012; Sánchez Maldonado et al., 2014). Chlorogenic acid is an ester of the caffeic and (-)-quinic acid and it is reported that esterification of caffeic acid by a sugar moiety decreases its antioxidant activity (Cuvelier et al., 1992). Studies show that chlorogenic acid is less effective as an antioxidant than caffeic acid in lard and stripped corn oils (Chen & Ho, 1997). At concentrations of 0.5, 1.0 and 2.0 mM, caffeic was more effective against alkoxyl radical scavenging in sunflower oil (Milic et al., 1998) and better inhibited lipid oxidation in fish muscles (Medina et al., 2007). Contrary, it is possible that the binding of the quinic acid to caffeic acid increases antioxidant activity and decreases hydrogen peroxide and $DPPH^{\bullet}$ scavenging activities (Sroka & Cisowski, 2003). Marinova et al. (2009) had found that difference in the antioxidative activity of chlorogenic and caffeic acids during antioxidation of triacylglycerols of sunflower oil strongly depends on their concentrations and at 2.8×10^{-4} M both acids show equal effectiveness and strength, but at concentrations above 10×10^{-4} M caffeic acid is much more effective and stronger inhibitor. Marinova et al. (2009) explained this phenomenon with two reasons: a) there are specific interactions of the acids and b) the participation of radicals derived from chlorogenic acid on more than one reaction of chain propagation, while the radicals of caffeic acid participate in one reaction.

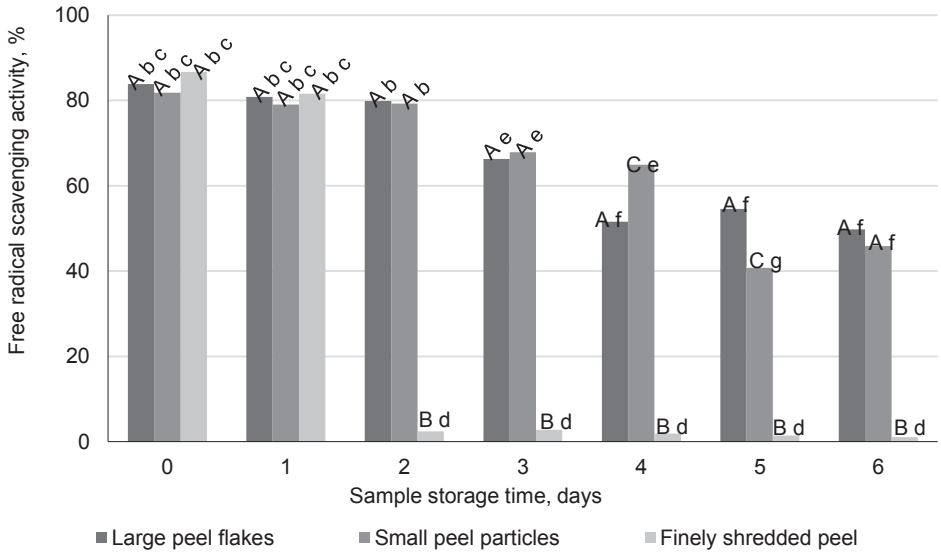

Figure 2. Effect of the storage time at uncontrolled conditions on the free radical scavenging activity of the potato peel extracts. The data is presented as a mean (n = 9). Similar lowercase letters indicate no significant difference among samples ($P \leq 0.05$); similar uppercase letters indicate no significant difference among peel types within each day separately ($P \leq 0.05$).

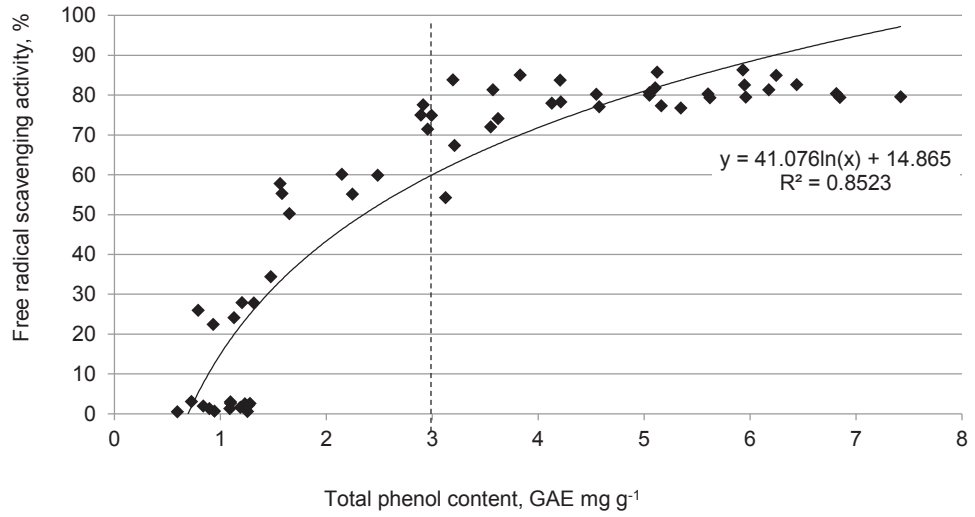

Figure 3. Correlation between total phenol content and the free radical scavenging activity.

Usually, chlorogenic acid is most abundant in PP, but when PP are stored at room temperature or in light, chlorogenic acid degrades and transforms into caffeic and quinic acids (Sotillo et al., 1994). Based on the collected data it can be assumed, that after peeling there were big amounts of chlorogenic acid in the samples. When total amount of polyphenols started to decrease, chlorogenic acid degraded and caffeic acid was released in sufficient amount to hold antiradical activity of the extract on the high level till the total phenol content did not decrease below 3.0 mg g^{-1} GAE (Fig. 3) when caffeic acid concentration became too low.

Combining data of total polyphenol content and antiradical activity, it is concluded that larger PP wastes can be stored in the plastic open containers at 20 ± 3 °C in open air without additional aeration for up to two days without significant changes in the total polyphenol amounts and antiradical activity. Finely shredded PP is easily exposed to the microbial and fermentative degradation and should not be stored at the same conditions longer that one day.

CONCLUSIONS

Results show that larger peel samples, large flakes and small peel particles, can be stored in the plastic open containers at 20 ± 3 °C in open air without additional aeration for up to two days without significant changes in the total polyphenol amount and antiradical activity. Starting with the third day, total phenol amount in the both peel sample types decreased in average by 40%, comparing to the previous day. Finely shredded peel show significant decrease in the total phenol amount, by 66%, and in the antiradical activity, by 97%, already on the second day of the storage. This fact indicates that in the finely shredded peel samples phenols are easily accessible to the oxidative and fermentative processes. Based on the results, if there are no special conditions for the storage of the potato peel wastes at the processing plant, for the efficient phenol extraction purpose it is recommended to store the whole solid peel material, that is not

grinded, no longer than for two days. Meanwhile, finely shredded peel must not be stored more than one day. Acquired results make a basis for the upcoming study on the application of the potato peel wastes and its extracts in the food production.

ACKNOWLEDGEMENTS. The present study was supported by the Latvian State Research program 'Agricultural Resources for Sustainable Production of Qualitative and Healthy Foods in Latvia (AgroBioRes)' (2014–2017). Project No. 4 'Sustainable use of local agricultural resources for qualitative and healthy food product development (FOOD)'.

REFERENCES

Ahokas, M., Välimaa, A.-L., Lötjönen, T., Kankaala, A., Taskila, S. & Virtanen, E. 2014. Resource assessment for potato biorefinery: Side stream potential in Northern Ostrobothnia. *Agronomy Research* **12**(3), 695–704.

Albishi, T., John, J.A., Al-Khalifa, A.S. & Shahidi, F. 2013. Phenolic content and antioxidant activities of selected potato varieties and their processing by-products. *Journal of Functional Foods* **5**(2), 590–600.

Al-Weshahy, A. & Rao, V.A. 2009. Isolation and characterization of functional components from peel samples of six potatoes varieties growing in Ontario. *Food Res. Int*. **42**(8), 1062–1066.

Amado, I.R., Franco, D., Sánchez, M., Zapata, C. & Vázquez, J.A. 2014. Optimisation of antioxidant extraction from *Solanum tuberosum* potato peel waste by surface response methodology. *Food Chem*. **165**, 290–299.

Cardoso, L.C., Serrano, C.M., Quintero, E.T., López, C.P., Antezana, R.M. & Martínez de la Ossa, E.J. 2013. High pressure extraction of antioxidants from *Solanum stenotomun* peel. *Molecules (Basel, Switzerland)* **18**(3), 3137–3151.

Chen, J.H. & Ho, C.T. 1997. Antioxidant activities of caffeic acid and its related hydroxycinnamic acid compounds. *J. Agr. Food Chem*. **45**(7), 2374–2378.

Cuvelier, M.E. Richard, H. & Berset, C. 1992. Comparison of the antioxidant activity of some acid-phenols: Structure-activity relationship. *Biosci. Biotech. Bioch*. **56**(2), 324–325.

Directive 2008/98/EC if the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives. 2008. Referred 08.12.2015. Available at: http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32008L0098&from=EN.

FOASTAT, compare data, potatoes, worldwide. 2013. Referred 06.12.2015. Available at: http://faostat3.fao.org/compare/E.

Jung, J.K., Lee, S.U., Kozukue ., Levin, C.E. & Friedman, M. 2011. Distribution of phenolic compounds and antioxidative activities in parts of sweet potato (Ipomoea batata L.) plants and in home processed roots. *J. Food Compos. Anal*. **24**(1), 29–37.

Koduvayur Habeebullah, S.F., Nielsen, N.S. & Jacobsen, C. 2010. Antioxidant activity of potato peel extracts in a fish-rapeseed oil mixture and in oil-in-water emulsions. *J. Am. Oil Chem. Soc*. **87**, 1319–1332.

Luthria, D.L. 2012. Optimization of extraction of phenolic acids from a vegetable waste product using a pressurized liquid extractor. *Journal of Functional Foods* **4**(4), 842–850.

Makris, D.P., Boskou, G. & Andrikopoulos, N.K. 2007. Polyphenolic content and in vitro antioxidant characteristics of wine industry and other agri-food solid waste extracts. *J. Food Compos. Anal*. **20**(2), 125–132.

Mane, S., Bremner, D.H., Tziboula-Clarke, A. & Lemos, M.A. 2015. Effect of ultrasound on the extraction of total anthocyanins from Purple Majesty potato. *Ultrason. Sonochem*. **27**, 509–514.

Mansour, E.H. & Khalil, A.H. 2000. Evaluation of antioxidant activity of some plant extracts and their application to ground beef patties. *Food Chem*. **69**(2), 135–141.

Marinova, E.M., Toneva, A. & Yanishlieva, N. 2009. Comparison of the antioxidative properties of caffeic and chlorogenic acids. *Food Chem*. **114**(4), 1498–1502.
Mattila, P. & Hellström, J. 2007. Phenolic acids in potatoes, vegetables, and some of their products. *J. Food Compos. Anal*. **20**(3–4), 152–160.
Medina, I., Gallardo, J.M., Gonzalez, M.J., Lois, S. & Hedges, N. 2007. Effect of molecular structure of phenolic families as hydroxycinnamic acids and catechins on their antioxidant effectiveness in minced fish muscle. *J. Agr. Food Chem*. **55**(10), pp. 3889–3895.
Milic, B.L., Djilas, S.M. & Candovic-Brunet, J.M. 1998. Antioxidative activity of phenolic compounds on the metal-ion breakdown of lipid peroxidation system. *Food Chem*. **61**(4), 443–447.
Murniece, I., Tomsone, L., Skrabule, I. & Vaivode, A. 2014. Carotenoids and Total Phenolic Content in Potatoes with Different Flesh Colour. In E.Straumite (ed.) 9th Baltic Conference on Food Science and Technology 'Food for Consumer Well-Being' FOODBALT 2014 Conference Proceedings. LLU, Jelgava, pp. 206–211.
Nayak, B., Berrios, J.D.J., Powers, J.R., Tang, J. & Ji, Y. 2011. Colored potatoes (*Solanum tuberosum* L.) dried for antioxidant-rich value-added foods. *J. Food Process. Pres*. **35**, 571–580.
Pasqualone, A., Bianco, A.M. & Paradiso, V.M. 2013. Production trials to improve the nutritional quality of biscuits and to enrich them with natural anthocyanins. *CyTA - Journal of Food* **11**(February 2015), 301–308.
Sabeena Farvin, K.H., Grejsen, H.D. & Jacobsen, C. 2012. Potato peel extract as a natural antioxidant in chilled storage of minced horse mackerel (*Trachurus trachurus*): Effect on lipid and protein oxidation. *Food Chem*. **131**(3), 843–851.
Sánchez Maldonado, A.F., Mudge, E., Gänzle, M.G. & Schieber, A. 2014. Extraction and fractionation of phenolic acids and glycoalkaloids from potato peels using acidified water/ethanol-based solvents. *Food Res. Int*. **65**, 27–34.
Schieber, A. & Saldaña, M. 2009. Potato Peels : A Source of Nutritionally and Pharmacologically Interesting Compounds – A Review. *Food* **3**(2), *Global Science Books*, pp. 23–29.
Shah, M.A., Bosco, S.J.D. & Mir, S.A. 2014. Plant extracts as natural antioxidants in meat and meat products. *Meat Sci*. **98**(1), 21–33.
Singh, N., Kamath, V., Narasimhamurthy, K. & Rajini, P.S. 2008. Protective effect of potato peel extract against carbon tetrachloride-induced liver injury in rats. *Environ. Toxicol. Phar*. **26**(2), 241–246.
Singh, N. & Rajini, P. 2004. Free radical scavenging activity of an aqueous extract of potato peel. *Food Chem*. **85**, 611–616.
Singh, N. & Rajini, P.S. 2008. Antioxidant-mediated protective effect of potato peel extract in erythrocytes against oxidative damage. *Chem.-Biol. Interact*. **173**(2), 97–104.
Singh, P.P. & Saldaña, M.D.A. 2011. Subcritical water extraction of phenolic compounds from potato peel. *Food Res. Int*. **44**(8), 2452–2458.
Sroka, Z. & Cisowski, W. 2003. Hydrogen peroxide scavenging, antioxidant and anti-radical activity of some phenolic acids. *Food Chem*. Toxicol. **41**(6), 753–758.
Sotillo, D. R., Hadley, M., Holm, & E. T. 1994. Potato peel waste: stability and antioxidant activity of a freeze-dried extract. *J. Food Sci*. **59**, 1031–1033.
Thygesen, P., Dry, I. & Robinson, S. 1995. Polyphenol oxidase in potatoe. *Plant Physiol*. **109**, 525–531.
USDA, Basic Report: 11362, Potatoes, raw, skin. 2015. Referred 06.12.2015. Available at: http://ndb.nal.usda.gov/ndb/foods/show/3090?manu=&fgcd=.
Vamos-Vigyazo, I. 1981. Polyphenol oxidase and peroxidase in fruits and vegetables. *Crit. Rev. Food Sci*. **15**, 49–127.
Wijngaard, H.H., Ballay, M. & Brunton, N. 2012. The optimisation of extraction of antioxidants from potato peel by pressurised liquids. *Food Chem*. **133**(4), 1123–1130.

Wu, Z.-G., Xu, H.-Y., Ma, Q., Cao, Y., Ma, J.-N. & Ma, C.-M. 2012. Isolation, identification and quantification of unsaturated fatty acids, amides, phenolic compounds and glycoalkaloids from potato peel. *Food Chem*. **135**(4), 2425–2429.

Yu, L., Haley, S., Perret, J., Harris, M., Wilson, J. & Haley, S. 2003. Antioxidant properties of bran extracts form Akron wheat grown at different locations. *J. Agr. Food Chem*. **51**, 1566–1570.

Zia-Ur-Rehman, Habib, F. & Shah, W.H. 2004. Utilization of potato peels extract as a natural antioxidant in soy bean oil. *Food Chem*. **85**(2), 215–220.