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# Comparison of phenolic compounds and antioxidant activity of fresh and freeze-dried potatoes

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**Abstract.** Potatoes (*Solanum tuberosum* L.) contain a wide range of compounds with health benefits, and different techniques have been developed for the determination of these compounds. Freeze-drying is a common method for the preservation and preparation of samples for the analyses of bioactive compounds, but it is well known that drying influences the composition of food products. The aim of the current study was to compare phenolic compounds and antioxidant activity of fresh and freeze-dried potatoes. In the experiment 11 cultivar potatoes grown in experimental fields of the Institute of Agricultural Resources and Economics in 2016 were analysed. Potatoes were freeze-dried. Homogenized fresh and freeze-dried samples were extracted with an ethanol/water (80/20 w/w) solution. Total phenolic content (TPC) was determined using the Folin-Ciocalteu method, and the antioxidant activity was evaluated using 2,2-diphenyl-1-picrylhydrazyl (DPPH˙) and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) assays. The highest TPC and radical scavenging activity were determined in cultivars ‘Peru Purple’ and ‘Blue Congo’ potatoes. Freeze-drying influenced all the tested parameters but more significantly the TPC, and for certain cultivars a reduction of more than 30% was observed. A strong correlation between TPC, DPPH and ABTS in fresh and freeze-dried samples was observed, $r = 0.81$, $r=0.93$, $r = 0.92$, respectively. It could be concluded that the effect of freeze-drying on TPC and antioxidant activity is cultivar dependent.

**Key words:** potatoes, phenolic compounds, antioxidant activity, freeze-drying.

## INTRODUCTION

Potato (*Solanum tuberosum* L.) is one of the most widely grown and consumed crop in the world that contains many dietary valuable compounds (Leo et al., 2008). Potatoes are a source of carbohydrates, proteins and minerals which makes them a vital part of the human diet (Casanas et al., 2002). They are highly recommended as a part of everyday diet because many of the potatoes’ compounds have a beneficial effect on human health (Bravo, 1998; Katan & Roos, 2004). In addition, potatoes also contain secondary metabolites phenolic compounds which are highly beneficial for health (Velioglu et al., 1998; Espin et al., 2000; Manach et al., 2004). They are valuable phytochemicals which present antioxidant, anticarcinogenic, antibacterial, antiinflammatory, antiglycemic, antiviral and vasodilatory properties (Duthie, Duthie & Kyle, 2000; Reyes, Miller & Zevallos, 2005; Mattila & Hellstrom, 2006; Leo et al., 2008).

Phenolic compounds are a group that consists of thousands of different compounds and some of which, in addition to the above listed qualities; also have a positive effect on longevity, mental health, cardiovascular system and ocular organs (Parr & Bolwell, 2000; Manach et al., 2004; Scalbert et al., 2005). A high correlation has been found between the presence of phenolic compounds in potatoes and the total antioxidant capacity (Andre et al., 2007). Potatoes as a phenolic compound source are the third consumed crop after apples and oranges (Chun et al., 2005). Total phenolic content in potatoes is significantly higher ranging from approximately 530 to 1,770 mg 1 $kg^{-1}$ fresh weight (Al Saikhan, Howard & Miller, 1995), that is why the studies on the phenolic compound and antioxidant properties in context of potatoes are highly important. Phenolic compounds can be found in potatoes' flesh and skin, although the skin contains the highest concentration (Lewis, Walker & Lancaster, 1999; Nara et al., 2006). All potato cultivars have phenolic compounds, but some of them contain different total amounts, for example, red and purple flesh potato cultivars have twice as much total phenolic content compared to white flesh potatoes (Ezekiel et al., 2013), and also the technological process affects potatoes with different colour flesh differently (Brown et al., 2005; Reyes & Zevallos, 2003). For example, freeze-drying of purple flesh potatoes neither significantly affects total phenolic neither content nor total antioxidant content (Nayak, 2011). Although potatoes are naturally rich in phenolic compounds having high antioxidant activity, this factor can change based on conditions (storage, wounding, technological processes) to which potatoes are exposed.

The aim of this study was to evaluate and compare phenolic compound and antioxidant activity changes of fresh and technologically affected (freeze-drying) potatoes.

## MATERIALS AND METHODS

### Raw materials

The potatoes were planted in the middle of May and harvested in the last ten days of August or first days of September in 2016. The soil type in the field was sod-podzolic (PVv), sandy loam, pHKCl 5.3, organic matter 1.8%, contained $P_2O_5$ 120 mg $kg^{-1}$, $K_2O$ 143 mg $kg^{-1}$. Pre-crop – winter cereals, applied fertilisers before planting NPK 60:55:90 kg $ha^{-1}$ herbicides, insecticides and fungicides were applied according to conventional growing technology. Harvested tubers were kept in the storage facility at an air temperature of 4 °C and at a relative air humidity of 80 ± 5%. In the experiment eleven potato (*Solanum tuberosum* L.) cultivars with white, yellow and purple coloured flesh were evaluated (Table 1).

For the experiment a total of 10 kg (around 50–60 potato tubers) of table potato tubers per cultivar were selected into small piles, from ten different wooden boxes (the size of the box: 90 cm (l) ×50 cm (w) × 40 cm (h)). Five potatoes were selected from several location points of each box.

**Table 1.** Description of potato cultivars

| Cultivar | Breeder / country | Earliness | Tuber shape | Colour of skin | Colour of flesh |
|---|---|---|---|---|---|
| Imanta | AREI / Latvia | medium late | long oval | yellow with pink eyes | white |
| S 01085-21 | AREI / Latvia | early | oval | light yellow | light yellow |
| S 04009-37 | AREI / Latvia | medium late | oval | purple | white |
| Brasla | AREI / Latvia | medium late | round | yellow | yellow |
| Lady Claire | Meijer Research BV / The Netherlands | medium early | oval | cream | light yellow |
| Lenora | AREI / Latvia | medium early | round oval | yellow | yellow |
| Gundega | AREI / Latvia | medium late | round | pink | yellow |
| 2000-49.82 | AREI / Latvia | medium late | round | yellow | light yellow |
| 19514.20 | AREI / Latvia | medium late | round oval | purple | white |
| Blue Congo | | late | oval | dark purple | purple |
| Peru Purple | | late | oval | dark purple | purple |

Cut potato tuber cubes (1 x 1 cm) were placed in a horizontal freezer (Zanussi, Pordenone, Italy) at a temperature of minus 18 °C before freeze-drying. Frozen potatoes were transferred to a freeze drier (CHRIST Alpha 2-4 LD plus, Osterode am Harz, Germany), which operates at the following conditions: temperature in a sample chamber – 83 ± 2 °C, vacuum – 1.0 mbar; freezing time – 34 hours.

**Chemical analysis**

Extraction of phenolic compounds from potatoes – the homogenized samples were extracted with ethanol (80/20 w/w) in a conical flask with a magnetic stirrer (magnet 4.0 cm × 0.5 cm) at 700 rpm for 1 h at room temperature (20 ± 1 °C). The extracts were then filtered (paper No.89). The extraction process was done in triplicate.

Determination of total phenolic content (TPC) – the TPC of potato extracts was determined according to the Folin-Ciocalteu spectrophotometric method (Singleton et al., 1999) with some modifications. The absorbance was measured at 765 nm and total phenolics were expressed as the gallic acid equivalents (GAE) 100 $g^{-1}$ dry weight (DW) of plant material.

Determination of antioxidant activity – antioxidant activity of potato extracts was measured on the basis of scavenging activities of the stable 2,2-diphenyl-1-picrylhydrazyl ($DPPH^{\bullet}$) radical as outlined by Yu et al. (2003). The absorbance was measured at 517 nm. The radical scavenging activity (RSA) of extracts was also measured by 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) ($ABTS^{\bullet+}$) radical cation assay (Re et al., 1999). For the assessment of extracts, the $ABTS^{\bullet+}$ solution was diluted with a phosphate buffer solution to obtain the absorbance of 0.800 ± 0.030 at 734 nm. The RSA was expressed as TE 100 $g^{-1}$ DW of plant material. The higher the Trolox equivalent antioxidant capacity (TEAC) of a sample, the stronger is the antioxidant activity.

**Statistical analysis**

Experimental results are means of three replications and were analyzed by Microsoft Excel 2010 (descriptive statistics) and SPSS 17.00 (ANOVA and correlation analysis). Analysis of variance (ANOVA) and Tukey's test were used to determine differences among samples. Differences were considered as significant at $p < 0.05$.

## RESULTS AND DISCUSSION

### Total phenolics

TPC of analysed potatoes ranged from 82–282 mg 100 $g^{-1}$ (Fig. 1) and presence of phenolics in potatoes complies with the previous studies indicating that potatoes contain highly health-beneficial phenolic compounds (Velioglu et al., 1998; Espin et al., 2000; Manach et al., 2004). Comparing TPC between tested potatoes, cultivar 'Blue Congo' showed the highest content. It is purple potato cultivar, and it has been evaluated that purple potatoes are one of the richest phenolics and anthocyanins source (Jansen & Flamme, 2006). Antioxidative activity in purple potatoes is demonstrated by anthocyanins (Reyes, Miller & Zevallos, 2005; Han et al., 2007; Steed & Truong, 2008). Purple potatoes compared to white potatoes have a higher health promoting effect and now are widely used as functional food in Europe, Southeast Asia and North America (Lei et al., 2014). In addition to acylated anthocyanins pigmented cultivars, for example, purple and red contains also greater levels of chlorogenic acid (the main phenolic acid in potatoes) compared to white and yellow-fleshed cultivars. While white and yellow-fleshed cultivars are more commonly used in human diet, this study highlights pigmented potatoes potential in contribution of higher amounts of phenolics and higher retention of valuable compounds during and after commercial processing. The latest studies suggest that that the usage of fresh or processed whole (unpeeled) potatoes provide higher levels of phenolics to human diet (Furrer et al., 2017).

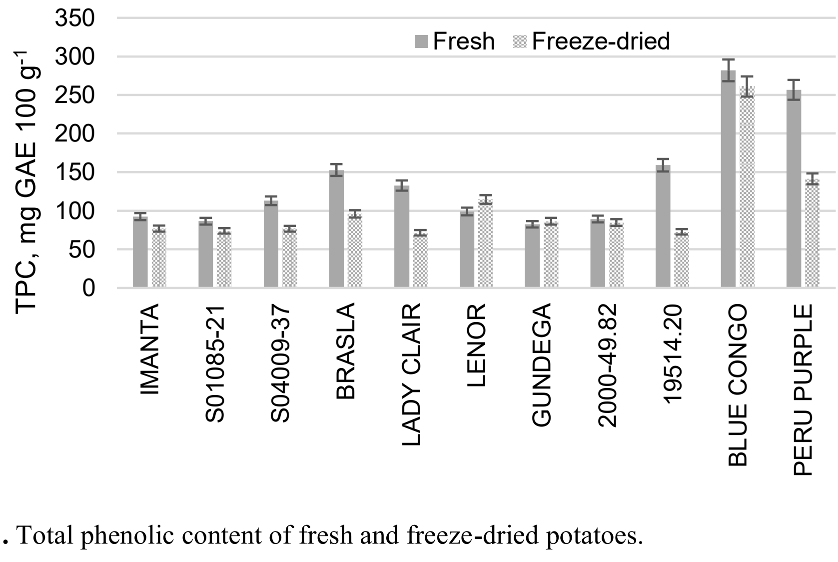


**Figure 1.** Total phenolic content of fresh and freeze-dried potatoes.

Phenolics and anthocyanins affect the colour of flesh and skin of potatoes forming a specific shade, i.e., red and purple potatoes. Potato flesh and skin can have different levels of pigmentation – entire pigmentation or partial. Potatoes with red colour flesh and skin contain acylated glucosides of pelargonidin, whereas potatoes with purple flesh and skin also contain acylated glucosides of delphinine, petunidin, malvidin, peonidin

(Brown, 2005). The availability of phytonutrients in potatoes nowadays is a highly important factor for consumers due to the increased focus on human health and a healthier diet which works as a developing force for future cultivar. Studies have indicated some potato cultivars that have significantly higher phytonutrients level compared to most widely used potato cultivars, also suggesting that focusing on potato selection with higher phytonutrients amount can raise the level of phytonutrients even more than it is now on average, for example, already identified are white-flesh potatoes with higher phenolics level compared to the average amount of phenolics in this colour potatoes, which proves that selection works well in the case of higher phytonutrients level (Navarre et al., 2011).

Technological processes, for example freeze-drying, affect the chemical content of plants (Angela & Meireles, 2009) so it is important that any kind of technological treatment is done using as low temperature as possible helping to retain as high biologically active compound levels as possible.

In all potato cultivars TPC after treatment was significantly lower compared to fresh samples and reduction was up till 45%.

**Antioxidant activity**

Antioxidant activity is closely linked to total phenolics and total anthocyanins (Reyes, Miller & Zevallos, 2005; Leo et al., 2008). In the current study 2,2-diphenyl-1-picrylhydrazyl (DPPH) scavenging activity ranged from 4.6–12.2 mM $100g^{-1}$ with the highest activity in potatoes 'Blue Congo' and 'Peru Purple' (Fig. 2). It also corresponds to other studies that state that antioxidant activity of fresh purple and red-fleshed potatoes is high (Cevallos-Casals & Cisneros-Zevallos, 2003).

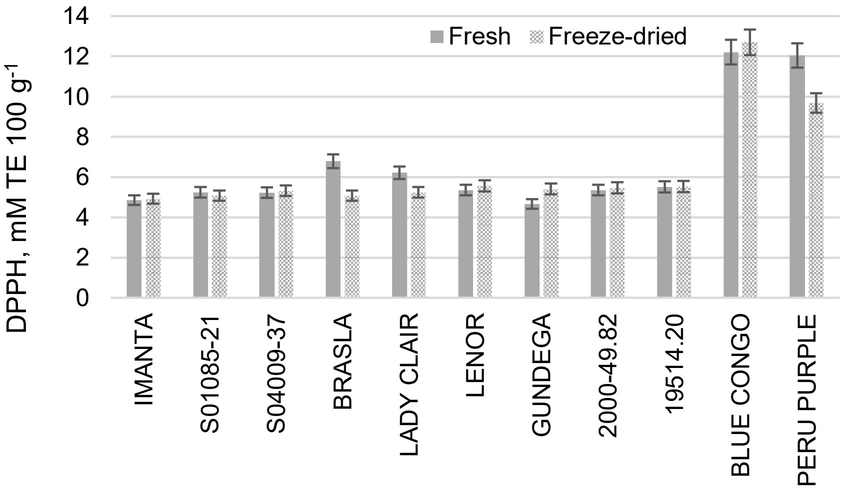


**Figure 2.** DPPH scavenging activity of fresh and freeze-dried potatoes.

Antioxidant activity is the ability of redox molecules in potatoes to encompass free radicals and taking into account the health promoting influence of all potatoes antioxidants it is important to study health-beneficial compounds (Puchau et al., 2010). Potatoes are considered to be a good source of antioxidants since they contain, for example polyphenols, ascorbic acid and $\alpha$-tocopherol (Yanishlieva-Maslarova & Heinonen, 2001).

Antioxidant activity is presented by some classes of biologically active compounds and compounds with such property could be used as an oxidation inhibitor (Jimenez et al., 2017). High costs of freeze-drying does not make it a widely used technological process, but it has some beneficial effects compared to other methods, for example, it helps retain phenolic compounds (Torres et al., 2010) and antioxidant activity (Chan et al., 2009; Zhao et al., 2017).

Potatoes 'Blue Congo' exhibited the highest antioxidant activity after freeze-drying, although generally in almost all freeze-dried samples no significant antioxidant activity reduction has been observed compared to fresh samples. Valadez-Carmona et al. (2017) reported increase in antioxidant activity after freeze drying of cacao, and explained it by extraction efficiency of electrons or hydrogen to stabilize the DPPH• turning them into intermediary stable radicals. The contribution of the sum of the bioactive phenolic compounds and flavonoids suggests that consumers could choose those cultivars with a high content of phenolic compounds and presumably high antioxidative properties. 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) scavenging activity ranged from 3–47 mM 100 $g^{-1}$ with the highest activity in 'Blue Congo' followed by 'Peru Purple' (Fig. 3). ABTS scavenging for ABTS cation scavenging temperature is a significant factor. The advantage of the ABTS radical is its high reactivity, and thus likely the ability to react with a broader range of antioxidants.

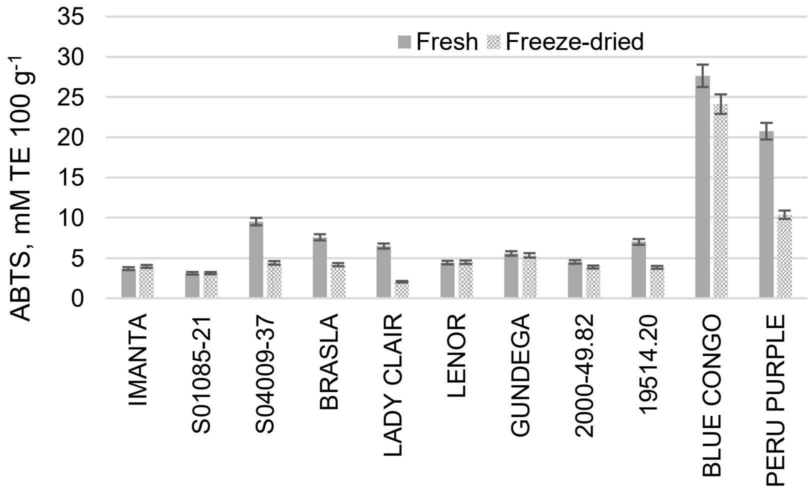


**Figure 3.** ABTS scavenging activity of fresh and freeze-dried potatoes.

On the other hand, the preparation of the ABTS reagent is more complicated and its stability is lower compared to DPPH (Marecek et al., 2017).

**Relationship between phenolic compounds and antioxidant activity**

Phenolic compounds have radical scavenging activity. Table 2 shows the Pearson`s correlation coefficients between the phenolic compounds levels and antioxidant activity in fresh and freeze-dried samples.

**Table 2.** Pearson`s correlation coefficients between antioxidant activity and total phenolic content of fresh and freeze-dried potatoes

| Parameters | Fresh | Freeze-dried | Significance level |
|---|---|---|---|
| Total phenolic content / 2,2-diphenyl-1-picrylhydrazyl (DPPH) | 0.96 | 0.95 | Substantial |
| Total phenolic content / 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) | 0.95 | 0.98 | Substantial |
| 2,2-diphenyl-1-picrylhydrazyl (DPPH) / 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) | 0.95 | 0.96 | Substantial |

Potato extracts evaluation presented a highly positive correlation between the content of phenolic compounds and antioxidant activity, thus the increase of one indicator will increase the other indicator. A strong correlation between antiradical activity and phenolic compounds was found in different potato materials.

## CONCLUSIONS

This study showed that cultivar and freeze-drying are significant factors affecting TPC, $DPPH^{\cdot}$ and $ABTS^{\cdot+}$ activity. The highest TPC and radical scavenging activity were determined in cultivars 'Peru Purple' and 'Blue Congo' potatoes. Freeze-drying caused the decrease of the content of phenolic compounds and antioxidant activity in potatoes. Freeze-drying influenced all the tested parameters but more significantly the TPC, and for certain cultivars a reduction of more than 30% was observed. A strong correlation between TPC, DPPH and ABTS in fresh and freeze-dried samples was observed, r = 0.81, r = 0.93, r = 0.92, respectively. It could be concluded that the effect of freeze-drying on TPC and antioxidant activity is cultivar dependent.

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