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Influence of gamma irradiation on volatile flavour profiles and physicochemical attributes of navel oranges (*Citrus sinensis* L.) under post-irradiation storage

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Abstract

The effects of irradiation at 0.5 – 2.0 kGy on physicochemical and volatile characteristics of navel oranges stored at 4°C were investigated. Fruit firmness was maintained when oranges were irradiated at 0.5 kGy, whereas samples irradiated at higher intensities exhibited lower firmness. The total soluble solids, titratable acidity, vitamin C content, total phenolic content and radical-scavenging activity were influenced by irradiation. However, at 0.5 and 1.0 kGy, these parameters were similar to those in non-irradiated control samples. These quality properties showed a significant decrease throughout the storage period. Principal component analysis (PCA) of the volatile pattern data obtained using electronic nose distinguished irradiated oranges from control fruits even after prolonged storage. The main volatile compounds, as determined using Kovats retention indices, were aldehydes and acetic esters at varying concentrations. Overall, irradiation doses of < 1.0 kGy had negligible effects on the quality properties of imported oranges. Appropriate dose range of gamma irradiation (0.5 – 1.0 kGy) proved very efficient, and the sensorial and nutritional qualities of navel oranges were maintained during extended storage of oranges at 4°C. These findings may be helpful in meeting guidelines of exporting irradiated foodstuffs especially navel oranges to facilitate international trade.

Introduction

Citrus is one of the most widespread fruit crops in the world that has great economic and dietetic significance. California is famous for the production of navel oranges, which are exported to many countries. In particular, the top five import markets, which imported 41% of the total crop in 2010, namely Japan, South Korea, Hong Kong, Canada and Australia (Elliot, 2017). Oranges have dietary importance as popular fruit owing to the presence of wide variety of phytochemicals such as flavonoids, vitamin C and carotenoids. However, high perishability of oranges due to the presence of high moisture contents makes them vulnerable to a wide range of diseases caused by microbial and insect pest attacks. Such diseases result in decreased shelf life and marketability of oranges (Cho *et al*., 2016).

Food irradiation could serve as a potential solution to overcome the problems hampering physicochemical qualities of fruits. Ionising radiation has been recognised as an effective tool for sterilisation purposes, because it disrupts deoxyribonucleic acid (DNA) molecule at a sub-cellular level and subsequently results in the termination of replication or death of the pest organisms (Diehl, 1990). However, the exposure of oranges to ionising radiation, in particular to the gamma rays, could impact their physicochemical quality attributes and volatile flavour profiles. This effect of ionising radiation on quality characteristics of navel oranges is dependent upon various factors namely type of cultivar, maturity stage of oranges, and applied dose level of gamma irradiation (Miller *et al*., 2000; McDonald *et al*., 2013). Jeong *et al*. (2016) have elucidated the effect of gamma irradiation for

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controlling post-harvest decay of satsuma mandarins caused by green mould to ensure microbial quality. Moreover, a negative impact on mandarin quality characteristics was avoided by employing a low dose (0.4 kGy) of gamma irradiation in combination with 10 ppm of sodium dichloro-s-triazinetrione. This combined treatment provided a synergetic effect to control green mould-induced decay by rupturing cell membranes. Therefore, gamma irradiation treatment has been suggested as an effective antifungal approach to ensure extended shelf life of satsuma mandarin fruits. In another study, Cho *et al*. (2016) investigated the effects of ionizing radiation (electron beam) at low dose levels (0.2 - 1.0 kGy) on antioxidant activities of navel oranges during storage. At such doses, radiation did not cause any notable changes in the levels of antioxidant compounds in comparison to their content in non-irradiated samples.

Irradiation treatment up to 1.0 kGy significantly extended the shelf-life of fruits, vegetables, and fresh-cut fruits by inhibiting ripening and microbial contamination (Fan *et al*., 2008). Moreover, the US Government (FDA, 1986) approved 1.0 kGy irradiation for the purpose of shelf-life extension as well as quarantine of fruits and vegetables. Irradiation treatment may cause foods to undergo both positive and negative changes in terms of modifications in their texture and contents of volatile components. These effects on physicochemical quality attributes determine the appeal or dislike of certain food products by consumers. Therefore, the present work was designed to determine the effects of low and high doses of gamma irradiation (0.5 - 2.0 kGy) on physiochemical and volatile characteristics of navel oranges stored at 4°C. Until now, only one study was conducted on radio-tolerance of gamma irradiated Lane Late' navel oranges for phytosanitary purpose (McDonald *et al*., 2013). To the best of our knowledge, the present work is the first to assess the changes in volatile and physicochemical characteristics of irradiated navel oranges of export quality during post-irradiation storage by employing electronic nose analysis for volatile profiles analysis, and principal component analysis was employed for elucidation of the numerical data trend of irradiated and non-irradiated samples.

Materials and methods

Oranges, irradiation and storage

Navel oranges (Sunkist Growers, Inc., California, USA) were purchased from a local market in Daegu, South Korea. Navel oranges were packed in cardboard boxes/pallets (Sunkist choice full carton: L × W × H = 17.06 × 11.38 × 10.75 in; approx. 40 lbs): 70 fruits/pallet, each fruit weighed 0.53 ± 0.03 lbs. Randomly selected 30 oranges were used for confirming whether or not they have been already irradiated before carrying out physicochemical experiments. The inorganic minerals from the samples were isolated following the steps described in European Commission (2001) and then thermoluminescence (TL) measurement was performed. Orange samples did not show any radiation-induced typical TL glow curves; TL peaks were in the range of 380–400°C with a weak intensity of 1.8 a.u. After confirming the irradiation status of orange samples in two days, the samples were used for further experiments. Oranges were randomly divided into four groups of approximately 140 oranges in each group. Four segregated groups of oranges were packed in the same-sized cardboard box (14.17 × 10.24 × 4.72 in) with the legible labelling and stored overnight at 4°C. Three groups of oranges were subjected to gamma irradiation at 0.5, 1.0 and 2.0 kGy, respectively, at a dose rate of 0.6 kGy/h. The fourth group received no irradiation but subjected to the same environmental conditions. Irradiation was carried out using a Co-60 gamma-irradiator (Nordion Int. Co. Ltd., Ottawa, Canada) at the irradiation facility of the Korean Atomic Energy Research Institute located in Jeongeup. Dosimetry measurements were carried out by alanine dosimeters (5 mm in diameters) to confirm the absorbed dose. Non-irradiated and irradiated samples were stored for six weeks at a storage temperature of 4 ± 1°C.

Firmness

A rheometer (Compac-100II, Sun Scientific, Tokyo, Japan) of the following specification — adapter no. 5 and 2 mm in diameter — was utilised for firmness determination. Interference was avoided by allowing removal of peel parts along the equator. Fruits were compressed by 10% of their diameters by applying pressure at a rate of 60 mm/min. Thirty randomly selected fruits were evaluated, and the results were expressed in g/cm^2.

Preparation of juice sample

Ten randomly selected fruits were peeled for juice extraction using a commercial juicer (HR-2870, Philips Co., Amsterdam, Netherlands). After centrifugation at 5,000 rpm for 20 min, the juice was filtered through a filter paper (Whatman No. 4, UK). Thereafter, the samples were stored at −18°C until further chemical analyses.

Total soluble solids and titratable acidity

A digital refractometer (Master-M, Atago, Tokyo, Japan) was used for measurements of total soluble solids (TSS). In addition, titratable acidity (TA) was measured by titration with 0.01 N NaOH at pH 8.2. The measurement was repeated three times, and the results were expressed as percent (%) of citric acid.

Vitamin C content

The vitamin C content was determined by high performance liquid chromatography (HPLC) (Agilent 1260 Infinity, Agilent Technologies, Santa Clara, CA, USA). Juice samples were filtered through filters (0.45 µm pore size) to remove non-dissolved particles. A µBondapak C18 column was used (3.9 × 300 mm, Waters Co., MA, USA). HPLC analysis was carried out at a flow rate of 1 mL/min at room temperature. The mobile phase consisted of 5 mM H2SO4, and the detection was carried out at 254 nm. The measurement was repeated thrice, and vitamin C concentrations were reported as mg/100 g.

Total phenolic content

The juice samples were analysed for their total phenolic content (TPC) by Folin-Ciocalteau colorimetric method as described by Singleton and Rossi (1965). Incubation time lasted for 120 min. Absorbance values of the samples were measured at 750 nm by means of a spectrophotometer (Optizen 2120UV, Mecasys Co. Ltd., Daejeon, Korea). The measurement was repeated thrice, and the results were recorded as mg of gallic acid equivalent per 100 g.

Determination of antioxidant activities

2, 2-diphenyl-1-picrylhydrazyl (DPPH) RSA was determined according to the method described by Blois (1958) with some modifications. Briefly, DPPH stock solution was diluted by the addition of 50% ethanol, and the absorbance was measured at 517 nm to obtain the absorbance value of 1.00 ± 0.02. DPPH stock solution of 5 mL was added to each sample (0.5 mL) and the mixture was incubated for 30 s at room temperature, during which radical reduction occurred. Next, the absorbance values were measured by a spectrophotometer at 517 nm. 2,2'-Azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS) RSA was determined following the method reported by Re *et al*. (1999). Briefly, ABTS stock solution was diluted with ethanol (94%, v/v) to obtain the absorbance value of 0.70 ± 0.02 at 743 nm. Then, 5 mL ABTS solution was mixed with 0.2 mL sample, and absorbance values were measured by a spectrophotometer at 743 nm by using a standard curve prepared on the basis of measurements in 25 - 400 µM solutions of (±)-6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (trolox). The measurement was repeated thrice, and the results were expressed in µM of trolox equivalent (TE).

Volatile component patterns determination by E-nose analysis

Volatile compounds of samples were evaluated by electronic nose (E-nose) analysis carried out using the HERACLES E-nose (Alpha M.O.S., Toulouse, France), which was integrated with classical gas chromatographic (GC) functionality and E-Nose olfactory fingerprint software. This E-nose system was equipped with a sampling system and a GC instrument that comprised two short columns of different polarities (DB5 and DB1701) along with two flame ionisation detectors. Juice sample (1 mL) was injected into a 20-mL headspace vial and capped with polytetrafluoroethylene/silicone septum (Supelco, Bellefonte, PA, USA). Vials were incubated at 40°C for 10 min with agitation at 500 rpm. Next, the accumulated gas was injected into the headspace of the GC system for C7–C30. Hydrogen circulating at a rate of 1 mL/min under constant flow mode was employed as carrier gas. Injector temperature was maintained at 200°C. Oven temperature was manipulated as follows: 40°C for 5 s; 4°C/s ramp to 270°C and holding period for 30 s. Careful optimisation of parameters was performed, and five sample replicates were analysed. For volatile component analysis, numerical data trend of the odour map was evaluated by principal component analysis (PCA).

Statistical analysis

Statistical analysis system (SAS) software (version 8.1) (SAS Inst. Inc., Cary, NC, USA) was employed for data analysis. The results were expressed as mean ± standard deviation. Differences between means were analysed by one-way analysis of variance (ANOVA), and their significance was evaluated by the Duncan's multiple range test. Differences were considered significant at $p < 0.05$. For volatile components analysis, numerical data trend was evaluated by PCA using specific AlphaSoft (Alpha M.O.S., France) software provided in the HERACLES E-nose system for statistical data processing.

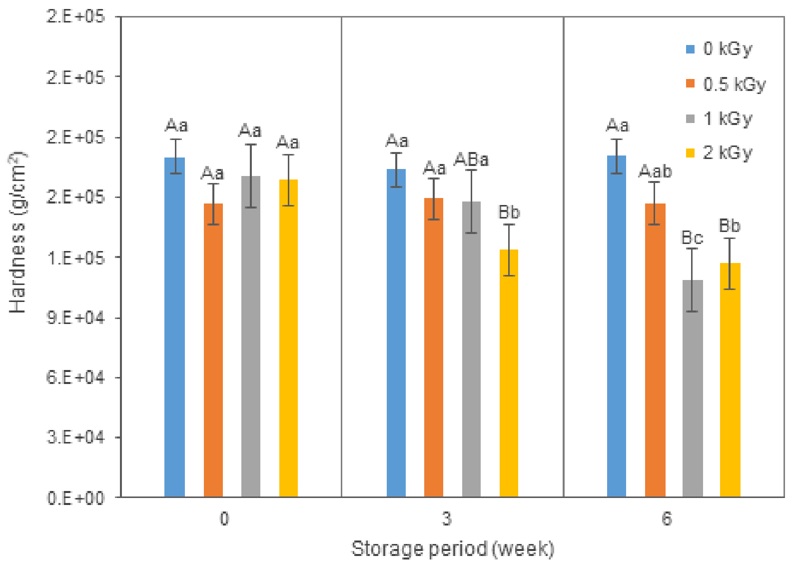

Figure 1. Changes in hardness (g/cm2) of gamma-irradiated oranges during storage at 4°C. Different uppercase within same storage period and different lowercase within same irradiation dose indicate significant difference at $p < 0.05$ by Duncan's multiple range test.

Results and discussion

Changes in firmness

Firmness has been reported to influence the acceptance and purchasing intention of consumers. Increased firmness has been reported to be positively correlated with consumers' acceptability (Gao *et al.*, 2011). In the present work, during a 6-week storage period, gamma-irradiated oranges gradually lost firmness in a radiation dose-dependent manner (Figure 1). Jung *et al.* (2015) have reported the dependence of firmness on storage and irradiation treatment. Firmness was found to be negatively correlated with applied irradiation dose and storage period. Ladaniya *et al.* (2003) have reported a lack of significant decrease in fruit firmness of 1.5 kGy irradiated Nagpur mandarins and sweet Mosambi oranges in comparison to the firmness of control samples. Firmness decreased significantly after 75 days of storage as compared to the firmness recorded at the start of the experiment. Moreover, a trend of decreasing firmness observed in the present work was found to be in agreement with previous reports (Kim and Yook, 2009). Radiation-induced reduction in firmness leads to fruit softening which is attributed to an overall reduction of total pectin content in fruit tissues (Jung *et al.*, 2015).

Table 1. Changes in total soluble solids (TSS), titratable acidity (TA), and TSS/TA ratio of gamma-irradiated oranges during storage at 4°C.

Property	Irradiation dose (kGy)	Storage period (week)		
		0	3	6
Total soluble solids (°Brix)	0	11.27 ± 0.23^{Aab}	11.40 ± 0.35^{Aa}	10.80 ± 0.24^{Ab}
	0.5	11.07 ± 0.23^{Aa}	11.13 ± 0.12^{Aa}	10.20 ± 0.30^{Bb}
	1	10.93 ± 0.23^{Aa}	10.80 ± 0.35^{Aa}	11.00 ± 0.20^{Aa}
	2	10.93 ± 0.12^{Aa}	11.00 ± 0.35^{Aa}	10.60 ± 0.32^{ABa}
Titratable acidity (%)	0	0.62 ± 0.03^{Aa}	0.55 ± 0.06^{Aa}	0.55 ± 0.03^{Aa}
	0.5	0.58 ± 0.03^{ABa}	0.58 ± 0.04^{Aa}	0.53 ± 0.03^{Aa}
	1	0.57 ± 0.03^{Ba}	0.53 ± 0.08^{Aa}	0.51 ± 0.02^{Aa}
	2	0.57 ± 0.03^{Ba}	0.49 ± 0.06^{Aa}	0.49 ± 0.03^{Aa}
TSS/TA ratios	0	18.29 ± 0.97^{Aa}	21.05 ± 1.87^{Aa}	19.57 ± 1.45^{Aa}
	0.5	19.25 ± 1.25^{Aa}	19.16 ± 1.76^{Aa}	19.32 ± 1.66^{Aa}
	1	19.37 ± 1.35^{Aa}	20.54 ± 2.99^{Aa}	21.55 ± 0.69^{Aa}
	2	19.05 ± 0.78^{Aa}	22.71 ± 3.47^{Aa}	21.61 ± 1.38^{Aa}

Different uppercase within a column and different letters within a row indicate significant difference at $p < 0.05$ by Duncan's multiple range test.

Changes in total soluble solids and titratable acidity

The effects of gamma irradiation on TSS, TA and TSS/TA ratio of oranges during storage are presented in Table 1. These quality characteristics in irradiated samples did not appear to be dose-dependently affected by the radiation throughout the storage period ($p < 0.05$). Moreover, samples analysed within the same storage week showed no marked variation and had TSS, TA and TSS/TA ratio values similar to those of control samples (0 week). Similar results have been previously reported which implied insignificant effects of the post-harvest storage period and irradiation treatment on TSS, TA and TSS/TA ratios. For example, in a study by Patil *et al*. (2004), TSS, TA and TSS/TA ratio values in irradiated grapefruit (*Citrus paradisi* Macf.) were not altered by 0.5 kGy irradiation when compared with control samples. Early season fruits did not show any significant changes in quality attributes which was attributed to applied irradiation treatment. However, decreases in TA, TSS and TSS/TA ratio values, relative to the values recorded in samples on day 0, were reported with the extension of the storage period over 35 days of storage.

Changes in vitamin C content

Among citrus fruits, orange is regarded as an important source of vitamin C for human consumption. Vitamin C serves as an important indicator of acceptable quality for intended consumers. Table 2 illustrates the effects of irradiation at different doses on vitamin C content in oranges during storage. Within the same storage group, irradiation treatment proportionally decreased vitamin C content to the applied dose (0 - 2 kGy) in comparison to that in control samples. All irradiated samples of all storage groups (0 - 3 weeks) demonstrated a decrease in vitamin C content by 9.55 - 10.81% as compared to the level measured in control samples at week 0. In addition, as far as the effect of storage was concerned, 3-week storage did not significantly reduce vitamin C content as compared to its levels at the start of experiment. However, vitamin C content became significantly lower ($p < 0.05$) after six weeks of storage in all irradiated samples in comparison with vitamin C levels at week 0, and a gradually decreasing trend was recoded with corresponding increases in applied irradiation doses from 0.5 to 2.0 kGy. Generally, these results agree with the data from previous studies (Joshi *et al*., 1990; Khalil *et al*., 2009). The possible cause of the gradual decline in vitamin C levels during post-harvest storage could be attributed to the enhanced respiratory activity in fresh fruits, which leads to accelerated enzymatic activity (possibly enzyme catalysed hydrolysis of 4-O-oxalyl-l-threonate) resulting in vitamin C degradation (Green and Fry, 2005). Ladaniya *et al*. (2003) have reported gradual decreases in vitamin C content in irradiated (1.0 - 1.5 kGy) mandarins and sweet oranges as compared to that in control samples. Vitamin C content decreased by 1.77% during 75 days of the post-irradiation storage period.

Table 2. Changes in vitamin C content (mg/100 mL) of gamma-irradiated oranges during storage at 4°C.

Irradiation dose (kGy)	Storage period (week)		
	0	3	6
0	55.68 ± 1.54^{Aa}	53.42 ± 2.49^{Aa}	45.56 ± 1.98^{Ab}
0.5	50.36 ± 0.56^{Ba}	51.13 ± 2.21^{Aa}	44.88 ± 3.08^{Aa}
1.0	49.66 ± 2.26^{Ba}	49.19 ± 1.60^{Aa}	43.41 ± 1.45^{Ab}
2.0	49.93 ± 2.57^{Ba}	48.87 ± 1.91^{Aa}	43.04 ± 1.97^{Aa}

Different uppercase within a column and different letters within a row indicate significant difference at $p < 0.05$ by Duncan's multiple range test.

Changes in total phenolic content

Table 3 illustrates the effect of gamma irradiation on TPC of oranges during storage. As compared to its value in control samples, TPC values in irradiated oranges tended to be negatively affected by irradiation, proportionally to the irradiation dose levels (0.5 – 2.0 kGy). In contrast to that in the samples stored for three weeks, the decrease of TPC in samples after six weeks of storage, relative to its value in control samples (week 0), was more significant ($p < 0.05$). Similar results have been previously reported. In particular, a similar decreasing trend of TPC values upon exposure to irradiation was reported in beans (Villavicencio *et al*., 2000) and Chinese cabbage (Ahn *et al*., 2005). In contrast, Oufedjikh *et al*. (2000) have reported increased TPC of gamma-irradiated Moroccan citrus fruits (*Citrus clementina* Hort. ex. Tanaka), which received an average applied dose of 0.3 kGy during 49 days of storage. That rise in TPC in irradiated fruits correlated with increased phenylalanine ammonia-lyase (PAL) activity, which could stimulate increased production of phenolic compounds. In addition, good evidence is available to demonstrate that radiation induced a decrease in polyphenol oxidase (PPO) activity as reported by Hanotel *et al*. (1995) which resulted in subsequent browning of fruits and vegetables. Both PPO activity and browning demonstrated negative correlation. Likewise, similar decreased activity of PPO has been reported in irradiated chicory (Tanaka and Langerak, 1975).

Table 3. Changes in total phenolic content (mg of gallic acid equivalent: GAE/100 mL) of gamma-irradiated oranges during storage at 4°C.

Irradiation dose (kGy)	Storage period (week)		
	0	3	6
0	70.83 ± 0.57^{Aa}	66.95 ± 2.64^{Ab}	41.23 ± 0.13^{Ac}
0.5	64.44 ± 3.42^{Ba}	61.39 ± 4.15^{Ba}	36.28 ± 0.23^{Cb}
1.0	60.33 ± 0.48^{Ca}	59.26 ± 0.80^{Ba}	37.72 ± 0.35^{Bb}
2.0	62.46 ± 1.91^{BCa}	58.88 ± 0.46^{Bb}	37.42 ± 0.23^{Bc}

Different uppercase within a column and different letters within a row indicate significant difference at $p < 0.05$ by Duncan's multiple range test.

Table 4. Changes in antioxidant activities of gamma-irradiated oranges during storage at 4°C.

Radical scavenging activity (RSA)	Irradiation dose (kGy)	Storage period (week)		
		0	3	6
DPPH (μM TE)	0	2,324 ± 24^{Ab}	2,418 ± 68^{Aa}	1,704 ± 3^{ABc}
	0.5	2,264 ± 51^{ABa}	2,164 ± 10^{Bb}	1,651 ± 40^{Bc}
	1.0	2,191 ± 65^{Ba}	2,086 ± 35^{BCb}	1,656 ± 33^{ABc}
	2.0	2,171 ± 83^{Ba}	2,064 ± 42^{Ca}	1,468 ± 6^{Cb}
ABTS (μM TE)	0	2,350 ± 4^{Aa}	2,096 ± 33^{Ab}	2,069 ± 31^{Ab}
	0.5	2,090 ± 35^{Ba}	1,817 ± 58^{Bb}	1,738 ± 42^{BCb}
	1.0	1,930 ± 24^{Ca}	1,815 ± 27^{Bb}	1,848 ± 56^{Bb}
	2.0	1,969 ± 50^{Ca}	1,761 ± 24^{Bb}	1,640 ± 92^{Cb}

Different uppercase within a column and different letters within a row indicate significant difference at $p < 0.05$ by Duncan's multiple range test.

Changes in antioxidant activities

Among fruits, oranges have been highlighted as a prominent source of antioxidant compounds. Antioxidants impart protective effects against various diseases, such as stroke, certain types of cancer, and cardiovascular diseases (Klimczak *et al*., 2007). Higher radical-scavenging properties in oranges have been attributed to the presence of polyphenolic compounds (flavonoids and hydroxycinnamic acids), ascorbic acid (vitamin C), and water soluble antioxidants (Gliszczynska-Swiglo *et al*., 2004). Soon after irradiation treatment, significant ($p < 0.05$) decreases in both DPPH and ABTS RSA values were observed in comparison with the parameters recorded in control samples (0 kGy). Moreover, storage period has also affected RSA, and oranges at three and six weeks of storage showed lower RSA values: DPPH and ABTS RSA values decreased by 26.68–36.83% and 11.96–30.21%, respectively, as compared to the measurements in control samples (Table 4). Lower TPC and vitamin C contents upon exposure to gamma irradiation might correlate with reduced RSA of irradiated oranges. Similarly, Breitfellner *et al*. (2002) have reported a reduction in the content of phenolic compounds (cinnamic, *p*-coumaric, gallic, and hydroxybenzoic acids) in strawberries irradiated at 1 - 10 kGy. Likewise, reductions in vitamin C and antioxidant activity have also been reported in sweet Mosambi oranges gamma-irradiated at 1.5 kGy (Ladaniya *et al*., 2003). Similar trend has been reported in kiwifruit (Actinidia deliciosa var. deliciosa cv. Hayward) gamma-irradiated at levels up to 3 kGy (Kim and Yook, 2009).

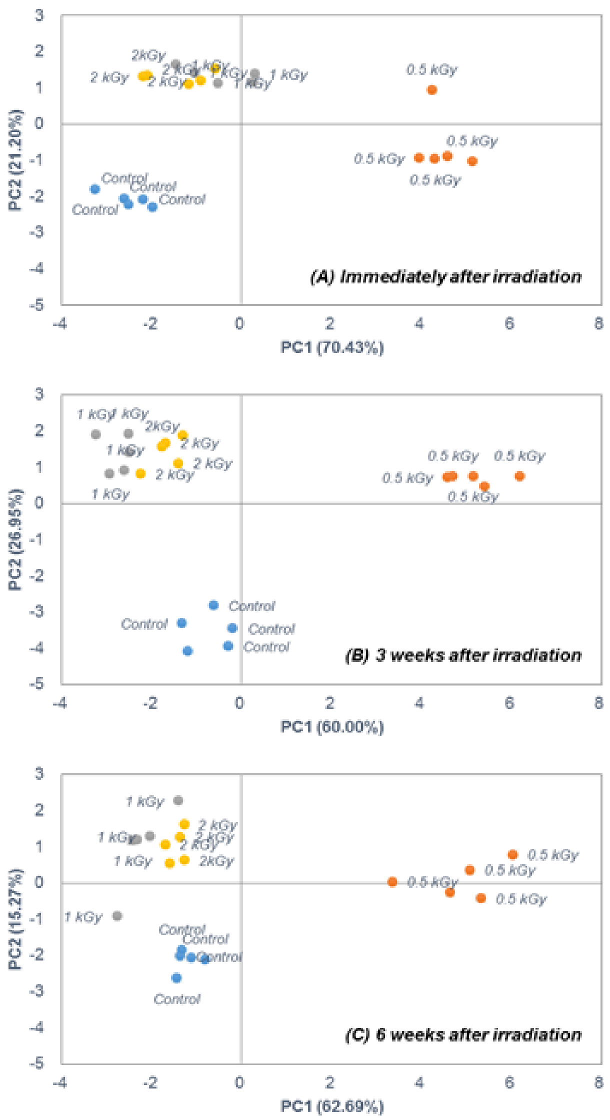

Figure 2. Principal component analysis of volatile flavour compound profiles in gamma-irradiated oranges using E-nose immediately after irradiation (A), after three weeks (B), and after six weeks (C) of post-irradiation storage at 4°C.

Changes in volatile component patterns by E-nose analysis

Oranges contain a wide variety of volatile components, which give special aromatic and flavour characteristics responsible for the particular orange flavour. These volatile compounds are found in a pattern of quantitative and interdependent relationships with each other. Important compounds contributing to this unique flavour include ketones, esters, aldehydes, terpenes and alcohols. In the present work, soon after the irradiation treatment by gamma rays, the presence of volatile compounds in oranges was determined by E-nose coupled with GC analysis. A quantitative data trend of volatile components present in irradiated oranges was elucidated by PCA technique that differentiated irradiated (0.5, 1.0, and 2.0 kGy) samples from non-irradiated counterparts (0 kGy) stored for different storage periods (Figure 2). As shown in Figure 2, samples irradiated at 0.5 and 1.0 kGy were clearly distinct from control samples (0 kGy). After orthogonal transformation by PCA in a 2D coordinate system, major variables contributing towards highest variability in dataset were plotted as principal components (PC1 and PC2). Soon after gamma irradiation treatment, PC1 accounted for 70.43% of total variation, whereas PC2 was responsible for only 21.20% of total variation. These results clearly show that irradiated oranges (0.5, 1.0 and 2.0 kGy) stored for different periods could be clearly distinguished from control samples (0 kGy) based on their volatile flavour profiles.

Possible volatile flavouring compounds were determined by searching and matching with a comprehensive library index known as "Kovats Index." Table 5 shows possible matches of characterised volatile compounds to those with similar Kovats Indices, also known as retention indices in terms of proportionate peak area, and their corresponding odour characteristics. The most prominent compounds found at the highest concentrations were propionaldehyde and limonene (classified as most abundant cyclic terpene in oranges). Irradiated orange samples had significantly ($p < 0.05$) higher concentrations of limonene as compared to control samples (0 kGy). Other main volatile compounds responsible for the fruity flavour

Table 5. Characterisation of volatile compounds (proportionate peak area) of gamma-irradiated oranges using E-nose immediately after irradiation.

RT in DB5(s)	Irradiation dose (kGy)				Possible matching compounds based on Kovats Index	Odour description
	0 kGy	0.5 kGy	1.0 kGy	2.0 kGy		
13.20	1,516 ± 41	1,554 ± 63	1,509 ± 41	1,556 ± 32	Trimethylamine	Fishy, oily, rancid, sweaty, fruity
13.86	2,566 ± 204	2,297 ± 187	2,307 ± 208	2,415 ± 217	Acetaldehyde	Pungent, ethereal, fresh
15.28	81,592 ± 3,283	87,435 ± 1,880	80,211 ± 3,231	87,067 ± 3,561	Propionaldehyde	Ethereal, pungent
16.50	1,709 ± 81	-	-	-	-	-
21.48	-	111 ± 5	164 ± 7	202 ± 19	-	-
22.44	808 ± 64	927 ± 45	757 ± 76	884 ± 66	Ethyl acetate	Ethereal, fruity, sweet, grape
35.01	2,193 ± 99	2,356 ± 63	2,054 ± 92	1,971 ± 81	Ethyl butyrate	Fruity juicy fruit pineapple cognac
44.77	277 ± 12	802 ± 34	433 ± 13	353 ± 25	2-Vinyl pyrazine	Nutty
47.34	1,102 ± 25	1,202 ± 380	1,602 ± 43	1,407 ± 50	Phenol	Phenolic plastic rubber
50.32	58,973 ± 1,487	166,710 ± 2,877	86,640 ± 2,652	76,001 ± 2,158	Limonene	Sweet, citrus
51.79	301 ± 16	849 ± 22	447 ± 48	368 ± 38	Acetophenone	Sweet, cherry pit
53.70	519 ± 74	1,194 ± 56	679 ± 109	601 ± 92	Linalool	Citrus, orange, floral, terpy
69.28	1,082 ± 193	1,127 ± 110	1,084 ± 48	1,174 ± 81	Hexyl hexanoate	Green, sweet, waxy, fruity
77.56	420 ± 21	343 ± 126	279 ± 47	342 ± 68	-	-

of oranges were considered to be ethyl butanoate, ethyl hexanoanate and octanal propionaldehyde (Birla *et al*., 2005). As far as the effect of irradiation on volatile flavour compounds is concerned, O'Mahony *et al*. (1985) have reported no significant changes in volatile flavour components of navel oranges following irradiation at 0.6 - 0.8 kGy. Above 1 kGy, slight changes in odour patterns of gamma-irradiated navel oranges were reported by the authors in comparison with odour profiles of control samples immediately after irradiation. Similarly, Lee *et al*. (2004) have identified volatile profile patterns of gamma irradiated red pepper powder treated at up to 7.0 kGy. The major identified volatile compounds in non-irradiated samples in that study were hexanoic acid-methyl ester and tetramethylpyrazine, whereas 1,3-di-tert butylbenzene was only detected in irradiated red pepper samples. The detection of 1,3 di-tert butylbenzene was explained by the migration of specific volatile compound from packaging material due to irradiation treatment. The odour profiles of non-irradiated and irradiated red pepper samples were successfully differentiated into discrete cluster groups depending on applied dose levels (0, 3.0, 5.0, and 7.0 kGy) by PCA.

Conclusions

Oranges are susceptible to various rots and moulds, so quarantine conditions for corresponding pests and insects are necessary. The physicochemical and electronic sensing (E-nose) characteristics were investigated to determine the effects of irradiation applied to navel oranges at 0, 0.5, 1.0, and 2.0 kGy during post-irradiation storage at 4°C. Fruit firmness was maintained in irradiated oranges up to 0.5 kGy, whereas irradiation at higher dose levels led to the loss of fruit firmness. The titratable acidity, vitamin C content, free sugar content, total phenolic content and radical-scavenging activity were influenced by irradiation. However, at lower applied doses of 0.5 and 1.0 kGy, no marked differences in quality attributes were detected in comparison to measurements obtained in non-irradiated control samples (0 kGy). These quality properties showed a significant decreasing trend throughout the storage period. Electronic nose coupled with principal component analysis proved to be a promising tool for the discrimination between control oranges and oranges irradiated even at the lowest dose of 0.5 kGy as a phytosanitary treatment dose. Overall, according to the sterilising and lethal doses determined for different stages of citrus rust mite, and considering the effect of irradiation on the vitamin C and total acid content of the oranges, it is concluded that irradiation doses of 0.5 – 1.0 kGy should be effective to control citrus rust mite with no adverse effects on selected nutrients. E-nose was useful for rapid identification of unknown suspicious samples based on volatile flavour patterns analysis.

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