Dose-Dependent Changes of Chemical Attributes in Irradiated Sausages

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Summary and Implications

To determine the effects of irradiation on the chemical attributes of sausages, TBARS values, volatile compounds, gas compounds, and hydrocarbons of vacuum-packaged sausages were analyzed during 60 d of refrigerated storage. A sulfur-containing volatile compound (dimethyl disulfide), a gas compound (methane), and radiation-induced hydrocarbons (1-tetradecene, pentadecane, heptadecane, 8-heptadecene, eicosane, 1, 7-hexadecadiene, hexadecane) were mainly detected in irradiated sausages, and the concentrations of the compounds were irradiation dose-dependent. Especially methane and a few hydrocarbons were detected only in irradiated sausages and their amounts were dose-dependent. On the other hand, TBARS values, other off-odor volatiles (carbon disulfide, hexanal), and gas compounds (carbon monoxide, carbon dioxide) were found both in irradiated and nonirradiated sausages. Therefore, it is suggested that irradiation-induced hydrocarbons (1-tetradecene, pentadecane, heptadecane, 8-heptadecene, eicosane, 1, 7-hexadecadiene, hexadecane), dimethyl disulfide, and methane can be used as markers for irradiated sausages.

Introduction

Food irradiation is currently used in about 40 countries to improve microbiological safety and shelf-life of foods. The basic principle of food irradiation is that the high energy electrons from irradiation sources break water molecule in biological materials and produce free radicals such as hydrated electrons, hydrogen radical, and hydroxyl radicals, which can react with food components (fatty acids, proteins, or amino acids). The free radicals generated by irradiation are the main compounds that kill pathogenic microorganisms contaminated in foods and initiate various chemical reactions causing potential quality changes in meat products.

Irradiation-induced quality changes in meat products include color changes, production of irradiation off-odor, and acceleration of lipid oxidation. The Food and Agriculture Organization of the United Nations, the International Atomic Energy Agency and the World Health Organization (FAO/IAEA/WHO) reported that low-dose irradiation (< 10 kGy) presents no toxicological hazard and introduces no special nutritional or microbiological changes; hence toxicological testing of foods so treated is no longer required. However, some consumers are concerned about the chemical reactions taking place in the food products by irradiation and the compounds produced as a result of the reactions while others are looking for the safety margins that irradiation can bring to their food products. Consumers would want to know what they are consuming. To provide freedom to consumers to choose the type of products they prefer, thus, informative labeling is needed. For the informative labeling, however, markers to identify irradiated foods should be developed. Identification of irradiated over non-irradiated foods is highly desirable and is required to comply with existing regulations.

Different types of meat products including sausages are approved for irradiation to control microbial growth and to extend their shelf-life in many countries. However, feasible and stable chemical parameters, which can be used as an irradiation marker for the processed meat such as sausages, has not been fully developed especially during the long-term storage conditions.

The objective of the present study was to determine the impact of irradiation on the production of radiation-induced chemicals or changes that can be used to as identification tools for irradiated sausages.

Materials and Methods

Commercial sausages (29% of fat content) made with turkey and pork were purchased from a local market and then re-packaged in oxygen-impermeable nylon/polyethylene bags (9.3 mL $O_2/m^2/24$ h at 0 °C), and stored overnight at 4°C before irradiation. The samples were irradiated at 0, 2.5, 5 or 10 kGy using a linear accelerator. Lipid oxidation was determined using the TBARS method, and gas compounds using GC, hydrocarbons by GC/MS, and volatiles using dynamic headspace GC/MS.

Statistical analysis

The data were analyzed by SAS software (SAS Institute, 2001). Student-Newman-Keul's multiple range tests were used to compare the significant differences of the mean values of treatments ($p < 0.05$). The relationship between irradiation dose and each parameter was evaluated using correlation coefficients.

Results and Discussion

Irradiation at 2.5 kGy or higher increased the TBARS values of sausages, but there were no significant differences among irradiated sausages with different irradiation doses (Table 1). After 60 d of refrigerated storage, the TBARS values did not increase in irradiated sausages, which can be attributed to the anaerobic storage conditions of the samples. The TRBARS increase in Non-irradiated sausages at 60 d was significant, but the increased was small. There was little TBARS difference between non-irradiated and irradiated sausages at 60 d. Therefore, TBARS values cannot be used as an indicator for determining irradiation doses, especially meat products were vacuum-packaged.

Irradiation increased many volatile compounds found in non-irradiated sausages and newly generated a few volatiles not found in non-irradiated (Table 2). Although all the volatile compounds detected in sausages are not described in the table, important newly generated volatiles by irradiation include carbon disulfide, dimethyl disulfide, and dimethyl trisulfide. Dimethyl disulfide, most dominant sulfur volatile, was only detected in irradiated sausages, and thus could be an excellent marker to distinguish irradiated sausages from non-irradiated. Even though there was no significant difference between 5 and 10 kGy samples, dimethyl disulfide showed a tendency to increase with irradiation dose. The production of sulfur volatiles in irradiated meats was highly dependent upon the environmental conditions during the storage, and the sulfur volatiles were very volatile and easily disappeared during storage under aerobic aerobic conditions. Considerable amounts of dimethyl disulfide, however, were still detected in irradiated sausages and the amounts were highly irradiation dose-dependent (R^2 = 0.9585) after 60 d of storage. The sausage samples in the present study were firstly vacuum-packaged and then irradiated, and thus the sulfur volatiles produced by irradiation remained inside the samples during storage.

The most representative volatile compounds increased by irradiation were aldehydes and hexanal was the most predominant aldehyde. Although hexanal was detected in all the sausage samples regardless of irradiation, the amounts detected were highly dose-dependent. In the TBARS values, there were no significant differences among irradiated sausages with different doses, but the amounts of hexanal showed clear differences by irradiation dose. After 60 d, the amounts of hexanal did not increase but they were still irradiation dose-dependent. As shown in TBARS values, the lipid oxidation did not progress much due to anaerobic storage conditions. Therefore, TBARS value or aldehydes cannot be considered as good marker for irradiated sausages, even though they show some tendencies of increase by irradiation.

Carbon monoxide was detected both in non-irradiated and irradiated samples and the amount produced showed dose-dependent trends. After 60 d of storage, however, the amounts of carbon monoxide increased in all samples and the dose-dependency decreased (Table 3). On the other hand, methane was found only in irradiated sausages with dose-dependent manner (R^2 = 0.9431). The dose-dependent production of methane was maintained during the 60 d of storage under vacuum conditions (R^2 = 0.9121). Methane was not detected in non-irradiated sausage at 60 d. The production of carbon dioxide was inconsistent in all samples. Therefore, methane can be used as an excellent irradiation marker for irradiated sausages.

The fatty acids of sausages were mainly composed of $C_{18:1}$ (33-38%), followed by $C_{18:2}$ (19-28%), $C_{16:0}$ (18-21%) and $C_{18:0}$ (7-9%), and their compositions were not changed by irradiation (data not shown). Hydrocarbons including 1-Tetradecene (C14:1), pentadecane (C15:0), heptadecane (C17:0), 8-heptadecene (C17:1), and eicosane (C20:5) were detected only in irradiated sausages (Table 4). 1, 7-Hexadecadiene (C16:2) was found only in sausages irradiated at > 5 kGy. Hexadecene (C16:1) was detected in non-irradiated samples but the amount increased as irradiation dose increased. Overall, the concentrations of hydrocarbons in sausages increased linearly with irradiation dose up to 10 kGy, but their profiles were not influenced by fat contents. The radiation-induced hydrocarbons decreased with storage but still were detectable even after 60 days of post-irradiation storage, resulting in very high correlation coefficients (R^2 = 0.9091~0.9977). In general sausages have more than 20% fat, and thus hydrocarbons can be used as irradiation marker for sausages.

Table 1. TBARS (mg malonaldehyde/kg) values of irradiated sausages during the storage at 4℃.

Storage time (day)	Irradiation dose (kGy)				Coefficient (R2)
	0	2.5	5	10	
0	$^{B}0.56^{1,b}$	$^{A}0.81^{a}$	$^{A}0.94^{a}$	$^{A}0.94^{a}$	0.6902
60	$^{A}0.81^{b}$	$^{A}0.80^{b}$	$^{A}0.89^{ab}$	$^{A}0.97^{a}$	0.9092

^{a,b}Means with the same superscripts in each row are not significantly different($p < 0.05$)

^{A,B}Means with the same superscripts in each column are not significantly different ($p < 0.05$)

Table 2. Volatile compounds (total ion counts x 10^4) of irradiated sausages during the storage at 4℃.

Irradiation dose (kGy)	Dimethyl disulfide		Hexanal		Carbon disulfide	
	Storage time (day)					
	0	60	0	60	0	60
0	$^{C}0^{a}$	$^{D}16^{a}$	$^{D}1{,}974^{a}$	$^{B}1{,}336^{a}$	0^{b}	$^{B}10{,}748^{a}$
2.5	$^{B}718^{a}$	$^{C}127^{b}$	$^{C}2{,}625^{a}$	$^{AB}2{,}766^{a}$	0^{b}	$^{A}16{,}102^{a}$
5	$^{A}1{,}111^{a}$	$^{B}170^{b}$	$^{B}2{,}988^{a}$	$^{A}2{,}978^{a}$	0^{b}	$^{A}18{,}368^{a}$
10	$^{A}989^{a}$	$^{A}322^{b}$	$^{A}7{,}274^{a}$	$^{A}3{,}541^{b}$	0^{b}	$^{B}12{,}012^{a}$
Coefficient (R^2)	0.76	0.86	0.76	0.88		0.05

^{a,b}Means with the same superscripts in each row are not significantly different ($p < 0.05$)

$^{A\text{-}D}$Means with the same superscripts in each column are not significantly different ($p < 0.05$)

Table 3. Gas compounds (ppm) of irradiated sausages during the storage at 4℃.

Irradiation dose (kGy)	CO		CH_4		CO_2	
	Storage time (day)		Storage time (day)		Storage time (day)	
	0	60	0	60	0	60
0	$^{D}3.63^{1,b}$	$^{D}75.3^{a}$	$^{C}0.00$	0.00	$^{B}242^{b}$	$^{A}35{,}770^{a}$
2.5	$^{C}7.20^{b}$	$^{C}101.7^{a}$	$^{C}0.83^{b}$	$^{C}14.0^{a}$	$^{B}272^{b}$	$^{A}15{,}839^{a}$
5	$^{B}14.97^{b}$	$^{A}232.3^{a}$	$^{B}2.87^{b}$	$^{B}39.7^{a}$	$^{A}613^{b}$	$^{A}26{,}682^{a}$
10	$^{A}16.1^{b}$	$^{B}165.7^{a}$	$^{A}4.10^{b}$	$^{A}50.0^{a}$	$^{AB}426^{b}$	$^{A}15{,}773^{a}$
Coefficient (R^2)	0.831	0.384	0.943	0.912	0.31	0.246

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$^{A\text{-}D}$Means with the same superscripts in each column are not significantly different ($p < 0.05$)

Table 4. Hydrocarbons (µg/g fat) of irradiated sausages during the storage at 4℃.

Irradiation dose (kGy)	C14:1		C15:0		C16:2		C16:1		C17:1		C17:0	
	Storage period (day)											
	0	60	0	60	0	60	0	60	0	60	0	60
0	$^{D}0.00$	$^{D}0.00$	$^{D}0.00$	$^{D}0.00$	$^{C}0.00$	$^{C}0.00$	$^{C}0.87^{a}$	$^{C}0.76^{b}$	$^{D}0.00$	$^{D}0.00$	$^{D}0.00$	$^{D}0.00$
2.5	$^{C}0.18^{a}$	$^{C}0.17^{a}$	$^{C}0.05^{a}$	$^{C}0.04^{a}$	$^{C}0.00$	$^{C}0.00$	$^{C}0.96^{a}$	$^{C}0.83^{b}$	^{C} $.09^{a}$	$^{C}0.39^{b}$	$^{C}0.43^{a}$	$^{C}0.35^{a}$
5	$^{B}0.99^{a}$	$^{B}0.24^{b}$	$^{B}0.87^{a}$	$^{B}0.16^{b}$	$^{B}2.20^{a}$	$^{B}0.67^{a}$	$^{B}1.25^{a}$	$^{B}0.98^{b}$	$^{B}2.40^{a}$	$^{B}0.84^{b}$	$^{B}1.17^{a}$	$^{B}0.82^{b}$
10	$^{A}2.06^{a}$	$^{A}0.61^{b}$	$^{A}1.87^{a}$	$^{A}0.72^{b}$	$^{A}5.72^{a}$	$^{A}1.74^{b}$	$^{A}2.15^{a}$	$^{A}1.14^{b}$	$^{A}3.74^{a}$	$^{A}1.55^{b}$	$^{A}2.68^{a}$	$^{A}1.34^{b}$
Coefficient (R^2)	0.97	0.98	0.95	0.91	0.94	0.94	0.94	0.98	0.97	0.99	0.99	0.98

^{a,b}Means with the same superscripts in each row are not significantly different ($p < 0.05$)

$^{A\text{-}D}$Means with the same superscripts in each column are not significantly different ($p < 0.05$)