IRRADIATION EFFECTS ON MEAT: A REVIEW

EFEITO DA IRRADIAÇÃO NA CARNE: UMA REVISÃO

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ABSTRACT

Food irradiation is a process exposing food to ionizing radiations such as gamma rays emitted from the radioisotopes ^{60}Co and ^{137}Cs, or, high energy electrons and X-rays produced by machine sources. Irradiation can induce formation of isooctane-soluble carbonyl compounds in the lipid fraction and acid-soluble carbonyls in the protein fraction of meat. Increasing irradiation dose increases these compounds however, cooking reduces them. Among the volatile components, 1-heptene and 1-nonene are influenced most by irradiation dose, and aldehydes (propanal, pentanal, hexanal) are influenced most by packaging type (aerobiose vs vacuum). Sulfur-containing volatiles formed from sulfur-containing compounds (primarily amino acids) also contribute to irradiation odor. Reducing the temperature during the irradiation process reduces the effects on odor/flavor because free radical generation and dispersion are reduced. Ultimately, radiolysis of water into free radical species may be the initiators of both lipid oxidation breakdown products and sulfur-containing volatiles responsible for irradiation odor. Methods to decrease the detrimental effects of irradiation include oxygen exclusion (vacuum packaging), replacement with inert gases (nitrogen) and addition of protective agents (antioxidants).

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RESUMO

A irradiação de alimentos é um processo que expõe o alimento às radiações ionizantes tais como os raios gama, emitidos pelos isótopos radiativos 60^{Co} e 137^{Cs}, ou, os elétrons de alta energia e os raios X. A irradiação pode induzir a formação de compostos de carbonil isooctano solúveis na fração do lipídio e carbonils solúveis nos ácidos da fração proteica da carne. A dose crescente da irradiação aumenta estes compostos, entretanto o cozimento pode reduzi-los. Entre os componentes voláteis, 1 heptene e 1 nonene são mais influenciados pela dose de radiação, e os aldeídos (propanal, pentanal, hexanal) são mais influenciados pelo tipo de embalagem (aerobiose vs vácuo). Os compostos voláteis sulfurosos formados a partir dos compostos sulfurosos (primeiramente amino ácidos) também contribuem para o odor do alimento irradiado. A redução da temperatura durante o processo da irradiação reduz os efeitos indesejáveis no odor/sabor, pois a geração e a dispersão de radicais livres são reduzidas. Finalmente, a radiólise da água pode ser o iniciador dos produtos de decomposição da oxidação dos lipídios e dos componentes voláteis responsáveis pelo odor do alimento irradiado. Os métodos utilizados para diminuir os efeitos prejudiciais da irradiação incluem a exclusão do oxigênio (embalagem a vácuo), a utilização de gases inertes (azoto) e a adição de agentes protetores (antioxidantes).

INTRODUCTION

Soon after the discovery of X-rays in 1896, they were used for sterilization, medical and dental diagnostics, and for treatment of di-

sease. By 1905, patents had been filed in the US (Patent No. 788480) and in Great Britain (Brit. Patent No. 1609) to use irradiation to improve the condition of food. In 1955, the US Army Medical Department began to assess the whether commonly consumed foods be safely irradiated (Brewer, 2009). In 1980, the Food and Agriculture Organization of the United Nations, the International Atomic Energy Agency and the World Health Organization (FAO/IAEA/WHO) sated that:

The irradiation of any food commodity up to an overall average dose of 1 Mrad (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 (WHO, 1981).

Subsequently, the FDA proposed that specified foods irradiated at dosages not exceeding 100 krad were to be considered safe. Based on the Food Additives Amendment of 1958 to the Federal Food, Drug, and Cosmetic Act of 1938, irradiation is regulated as a food additive. Information requirements for the FDA to establish safety (radiological, toxicological and microbiological) of particular irradiated products have been reviewed by Pauli & Tarantino (1995). Food processors must use FDA-approved sources defined in the Code of Federal Regulations CFR (21 CFR 179.26): gamma-rays from sealed ^{60}Co or ^{137}Cs units, accelerated electrons generated from machine sources (<10 MeV), or X-rays generated from machine sources (<5 MeV). Because irradiation-induced pathogen reduction is most effective if applied after packaging, the packaging materials must also be approved by the FDA as safe under the conditions of the process.

The maximum dose permitted for meat depends on the type (poultry vs red meat), and whether it is chilled or frozen. Irradiation of fresh and frozen poultry was approved in 1992; red meat irradiation was approved in 1997 (FSIS & Inspection Service, 1999). For pathogen reduction, a maximum of 4.5 kGy is permitted for uncooked, chilled red meat; 7.0 kGy is permitted for uncooked, frozen meat; 3.0 kGy is permitted for fresh or frozen poultry (Table 1).

However, the detrimental effects of irradiation on odor, flavor and color have been major roadblocks for effective use of this technology to extend shelf life and reduce pathogen loads of fresh meat. In an effort to optimize conditions to procedure high quality products, the study of irradiation processing parameters has been under way for some time (Brewer, 2009).

Table 1
Levels of irradiation permitted for food use

Dose level	Purpose	Product examples
Low dose (up to 1 kGy)	Kill parasites	Trichinae in pork
	Kill insects and larvae after harvest	Fruits, vegetables, wheat, flour
	Inhibit sprouting	Potatoes, garlic, onions
	Slow ripening	Non-citrus fruits and vegetables
Medium dose (1–10 kGy)	Pasteurization to eliminate spoilage organisms	Strawberries, grapes
	Pasteurization to eliminate food borne illness causing microbes	Fresh or frozen seafood, poultry (3 kGy) and meat (3.5 kGy, fresh; 7.0 kGy, frozen)
High dose (10–50 kGy)	Sterilize food for immunocompromised people Eliminate some viruses.	Pathogen-free hospital foods
	Decontaminate some food additives and ingredients	Spices (10 kGy), enzyme preparations (10 kGy), gums, aromatic substances (30 kGy)

Source: Food safety and inspection service. 1999. irradiation of meat food products. Federal register. 64. (264) 72150-72166. 9 CFR Parts 381 abd 424. Docket No. 97-076F.

THE IRRADIATION PROCESS

The process of irradiation has been reviewed by Brewer (2004; 2009) and Thakur & Singh (1994). Irradiation is electromagnetic energy which is the energy that holds atomic particles together. Change in the forces among atomic particles (protons, neutrons, electrons) results in destabilization of the atom. It re-stabilizes by emitting energy to re-balance the nucleus. Increasing the energy level of electrons leads to emission of that energy as the electrons return to their original energy levels. This electromagnetic energy and its emission are termed "radiation". This radiation can take several forms depending on the level of energy being released. Sufficient energy to move the atoms in another molecule, but insufficient to change them chemically, is "non-ionizing radiation". Sufficient energy to break chemical bonds is "ionizing radiation" – it has sufficient energy cause a particle (electron) to leave the atom producing an electron-deficient particle. The particle left behind has an imbalance between nuclear protons and orbital electrons. Low energy electromagnetic radiation occurs as very long wave lengths (microwave, radio waves); intermediate energy radiation occurs as visible light and heat; high energy radiation occurs as X-rays and Y-rays; very high energy radiation is emitted as radioisotopes decay (eg. Uranium; Fig. 1). High energy sources (X-rays, Y-rays, accelerated electrons) are "ionizing"; they can knock an electron from an atom creating ions or free radicals. Very high energy sources (radioactive substances) can split atoms, generate neutrons and produce radioactive by-products (Brewer, 2009).

The energy of Y-rays and X-rays can be transferred to other atomic particles. Y-rays do not ionize atoms directly but transfer energy to other atomic particles which interact with other materials to form ions. Y-rays can pass through living tissues without interacting with them because they are so high energy and so small. Y-rays are emitted from the nucleus of radioactive atoms; X-rays are emitted from the electron field (Efiok, 1996). Radionuclides approved for food irradiation, ^{137}Cs and ^{60}Co, produce Y-rays as they decay over time. They have short half lives (^{137}Cs = 30 yr; ^{60}Co = 5.2 yr) compared to radioisotopes (^{234}Ur = 25,000 yr).

Irradiation dose is measured in Grays, the amount of energy per unit mass. The amount of energy to which a food is exposed is expressed as the "radiation absorbed dose"(rad). 1 kGy raises food temperature by <0.5°F.

1 Gray = 1 joule of energy absorbed/kg food
1 Gray = 6200 billion MeV absorbed/kg food
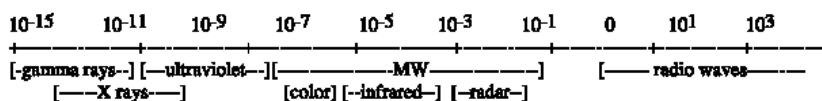1 Gray = 100 Rads (or 0.022 calorie/kg of food)
1 Rad = 100 erg/g.

Fig. 1. Electromagnetic spectrum—wavelength in meters (ICGFI, 1991).

Because of the energy input, irradiation can induce reactions among food components including: oxidation of metals and ions, oxidation/reduction of carbonyls to/from hydroxy derivatives, elimination of unsaturation (double bonds), decrease in aromaticity, hydroxylation of aromatic and heterocyclics, and generation of free radicals which can be oxidized to various peroxides. These reactions can initiate lipid oxidation, break down of protein components, and damage vitamins, color, odor, and flavor (Brewer, 2009).

Sources of irradiation energy

The radionuclides approved for food irradiation include ^{137}Cs and ^{60}Co. Radioactive cobalt (^{60}Co) decays to non-radioactive ni-

ckel by emitting α particles and γ-rays. The γ-rays kill rapidly growing cells (microbes) but do not leave the product radioactive (Lagunas-Solar, 1995). Because it is highly penetrating, it can be used to treat packaged food. Non-radioactive ^{137}Cs occurs in various minerals. It can be produced when uranium and plutonium absorb neutrons and undergo fission in a nuclear reactor, then decay to non-radioactive barium by emitting β particles and γ-rays (Brewer, 2009).

High energy particles can also be produced by "accelerating" electrons using electricity. These high energy, accelerated electrons are propelled out of an electron gun in a stream (e-beam). No radioactive source is required to produce accelerated electrons. They can penetrate 5-10 cm into food. X-rays can be produced by accelerating electrons into a thin metal plate (Satin, 2002).

Effect of fat content and lipid type

Irradiation results in volatile sulfur compounds responsible for the unique irradiation odor of ground beef. It also accelerates lipid oxidation on ground beef (Nam *et al*., 2003a). As far as the lipid fraction is concerned, unsaturated fatty acids are of primary concern. Because they are electron-deficient at the carbonyl groups and at the carbon double bonds, irradiation may result in formation of free radicals at these points (Thakur & Singh, 1994). Hydroxyl radicals (OH) tend to react with conjugated systems and are often considered to be the initiators of lipid oxidation in muscle tissue (Thakur & Singh, 1994). Autoxidation then proceeds via traditional pathways. The differents in total volatiles in irradiated pork patties has been reported to be due primarily to differences in aldehydes (Ahn *et al*., 1998a; Ahn *et al*., 1998b).

The volatile compounds responsible for the off-odor in irradiated meat produced by the impact of radiation on protein and lipid molecules are different from those of lipid oxidation alone (Jo & Ahn, 2000; Merritt *et al*., 1975). An increase in lipid peroxidation products (especially hexanal and trans-4,

5-epoxy-(E)-2-decenal) in combination with a loss of desirable meaty odorants (4-hydroxy-2, 5-dimethyl-3 (2H)-furanone and 3-hydroxy-4, 5-dimethy-2 (5H)-furanone) result in development of warmed over flavor of cooked, refrigerated beef (Kerler & Grosh, 1996). Du *et al*. (2001a) reported that irradiation of raw chicken breast produced alkanes and alkenes that appear to be result of both unsaturated fatty acid and amino acid breakdown.

Susceptibility of irradiated muscle tissues to lipid oxidation depends on endogenous characteristics of the tissue including the fat content, the fatty acid profile (proportion and degree of fatty acid unsaturation, and composition of phospholipids in the cell membrane) and the antioxidative potential of the tissue (Ahn *et al*., 1998b; Jo & Ahn, 2000). The most common fatty acids occurring in meat are oleic, linoleic, arachidonic, palmitc and stearic acids. Phospholipids constitute approximately 0.5-1% of the lean tissue (primarily phosphoglycerides) and a high proportion of unsaturated fatty acids that are susceptible to oxidation (Mottram, 1998). Phospholipids are also the source of several sulfides which are generated when they react with cysteine and/or ribose to produce mild, meaty beefy compounds (2-methyl-3-[methylthio] thiophene) (Rowe, 2002).

Whether or not fat content *per se* affects irradiation-induced oxidative changes is unclear. In beef, increasing fat level (from 11 to 22%) has been shown to increase 2-butanone, 2-pentanone and 3-hydroxy-2-butanone (El Magoli *et al*., 1996). The effect of irradiation on volatiles varies among muscle types within species which may be a function of fat content of the respective muscles. Pork patties from *L. dorsi* muscle (>6.5% fat) had higher Thiobarbituric Acid Reactive Substances (TBARS) and contained more propanal and pentanal after irradiation than did those from the *Psoas* (1.8% fat) and *R. femoris* (2.4% fat) muscles (Ahn *et al*., 1998a). On the other hand, Houben *et al*. (2000) found no difference in TBARS on irradiated lean (<1% fat) versus higher fat (~20% fat) minced beef. It

is likely that the unique fatty acid make-up of various meat species makes them more or less susceptible to irradiation-induced oxidation. Turkey and chicken dark meat contain similar amounts of linoleic acid (18:2; 1.75 and 1.87 g/100g lipid, respectively); (USDA National Nutrient Database for Standard Reference, 2007) and substantially more than is found in beef (0.12 g), pork (0.30 g), lamb (0.63 g), and Atlantic salmon (0.67 g). The total amount of 16:1, 18:1 and 18:2 is highest in chicken dark meat (5.33 g). It is similar in turkey white and dark meat, and Atlantic salmon (3.84, 3.34 and 1.82, respectively). These unsaturated fatty acids are primary source materials for lipid oxidation.

Autoxidation of linoleic acid produces, primarily, pentane, pentanal, hexanal, heptanal, (E)-2-heptanal, octanal, 1-octene, (z)-octanal, (E)-octanal, (E,Z)-2,4,-decadienal, wich produce grassy, rancid, fatty odors as well as lesser amounts 8-10 carbon aldehydes. The primary compound produced by autoxidation of linoleic acid is (E,Z)-2,4-heptadienal, which produces fishy, cooked meat odors, and lesser amounts of 2-10 carbon aldehydes. However, the odor thresholds of hexanal (1.7 μg; grassy, rancid) versus nonanal (13,500 μg; tallowy, fatty) make the relative contributions of these compounds to off-odors quite different (Belitz et al., 2004).

Because of the high concentration of dimethyl disulfide (cabage, putrid), 3-methylbutanal and 2-methylbutanal (rotten meat), and low concentrations of hexanal and pentanal (grassy, pungent), together with low TBARS, Du et al. (2002b) suggest that lipid oxidation immediately after irradiation is not the major contributor to off-odor of irradiated chicken.

Effect of antioxidants

Unless enzyme systems have been denatured, raw meat (unheated) has substantial antioxidant capacities (Ahn et al., 2000). Cooked meat is highly susceptible to oxidation because heat denatures antioxidant-forming systems and components, and damages cell structure exposing membrane lipids (phospholipids) to the environment (Ahn et al., 1998b). Antioxidants including free radicals scavengers (gallate, sesamol, tocopherol and butylated hydroxyanisole-BHA), metal chelators (ethylenediamine tetraacetic acid) and intrinsic antioxidants (carnosine) can reduce formation of off-odor volatiles in irradiated meat (Nam & Ahn, 2003).

Antioxidants can minimize irradiation-induced peroxidation of lard and tallow (Kyong et al., 1998; Kyong et al., 1999). Immediately after irradiation, ascorbyl palmitate (AP) was the most effective, followed by BHA, AP + α-tocopherol, and α-tocopherol alone. During storage, BHA was the most effective, followed closely by AP + α-tocopherol. AP was extremely effective in minimizing irradiation-induced oxidation in tallow, lard, and linoleic acid in a concentration-dependent fashion (Lee et al., 1999). Steady-state kinetic studies indicated that AP reduced oxidation by the oxygen-quenching mechanism. Adding ascorbic acid (0.1%) or sesamol + tocopherol (0.01%) to ground beef prior to irradiation can reduce generation of S-containing compounds (Nam et al., 2003a).

In some studies, inclusion of vitamin E (α-tocopherol) into animal diets has been shown to protect against lipid oxidation when meat is held in an oxygen-containing environment (Ahn et al., 1995; Houben et al., 2000). Vitamin E is retained in the membranes, in close proximity to phospholipids. Ahn et al. (1998c) reported that TBARS in irradiated turkey breast gradually decreased as dietary tocopherol acetate level increased.

Nam et al. (2003b) reported that these effects were dose-dependent. Dietary vitamin E protected irradiated, aerobically stored turkey meat against oxidative deterioration. The protective effect was dose-dependent; 100 IU vitamin E/kg diet was required to significantly reduce lipid oxidation. Similar findings associated with the natural vitamin E content of the lipid added to raw and cooked pork sausage (Jo & Ahn, 2000). However, Ohene-Adjei et al. (2004) reported that vitamin E-supplementation of swine diets had no effects on off-flavor of irradiated pork, initially

or during retail display. Galvin *et al*. (1998) reported that supplementation with 200 mg α-tocopherol decreased TBARS formation rate. Authors concluded that, in general, irradiation has little effect on lipid stability in α-tocopherol supplemented chicken following cooking and storage. Ahn *et al*. (1998c) reported that α-tocopherol supplementation decreased hexanal production in irradiated, stored turkey in a dose-dependent fashion. While dietary vitamin E can control lipid oxidation on irradiated raw turkey, Ahn *et al*. (1998c) reported that it was insufficient for oxidation control in irradiated, cooked meat during storage (aerobic packaging).

Dietary conjugated linoleic acid (CLA) has been shown to reduce TBARS, hexanal and pentanal formation in irradiated raw chicken (Du *et al*., 2000; Wiegand *et al*., 2001). It decreased TBARS, 18:3, and 18:1, and increased 18:0 and t, t-9, 11-isomers in the fat of irradiated beef patties derived from steers fed CLA (Wiegand *et al*., 2001). However, it was ineffective in maintaining volatile profiles (Du *et al*., 2001a; Du *et al*., 2001b; Du *et al*., 2002a). Irradiation accelerated lipid oxidation in aerobically packaged cooked chicken, but its effect was not as significant as that of packaging. Vacuum packaging almost completely protected lipids from oxidation and dramatically reduced volatile production in both irradiated and non-irradiated raw chicken samples (Du *et al*., 2000).

Added sesamol, quercetin and BHT are effective in controlling oxidation in both irradiated raw and cooked pork during storage (Chen *et al*., 1999). Sesamol + α-tocopherol (0.02%) added to pork patties prior to irradiation (4.5 kGy) has been shown to reduce TBARS in aerobically packaged pork during storage (Nam *et al*., 2002). Irradiation produced significant amounts of sulfur volatiles under vacuum packaging conditions. Propyl gallate + α-tocopherol reduced dimethyl disilfide and dimethyltrisulfide formation by > 50% and > 90%, respectiveliy, compared to the irradiated control (no antioxidant). These compounds disappeared after storage in aerobic conditions. Nam &

Ahn (2003) reported that the antioxidant-induced reduction of both lipid oxidation and production of sulfur volatiles was more apparent in vacuum packaged than in aerobically packaged pork. Of the antioxidants evaluated, sesamol was most effective, reducing dimethyl disulfide and total volatiles by 48% and 43%, respectively.

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