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**DOSE RATE EFFECT IN FOOD IRRADIATION: A REVIEW**  
**L'EFFET DE DÉBIT DE DOSE EN IRRADIATION DES ALIMENTS: UN EXAMEN**

**Harwant Singh**

**Whiteshell Laboratories**

**Pinawa, Manitoba R0E 1L0**

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AECL RESEARCH

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### ABSTRACT

Although most foods lose some vitamins and nutrients during processing and storage, food processing, including radiation processing, is generally carried out in a manner that minimizes nutrient loss and maximizes product safety. Radiation processing of foods at the doses recommended by the Codex Alimentarius Commission (up to 10 kGy) does not cause significant loss in their nutritional quality.

It has been suggested that the minor losses of nutrients associated with radiation processing may be further reduced by irradiating foods at the high dose rates generally associated with electron beams from accelerators, rather than at the low dose rates typical of gamma irradiation (e.g.,  $^{60}\text{Co}$ ). This review briefly examines available comparative data on gamma and electron irradiation of foods to evaluate these suggestions.

The potential beneficial effect of higher dose rates has been referred to as the dose rate effect (DRE). In the case of electron irradiation, some nutrients show lower loss than on gamma irradiation because of the DRE. For example, radappertized pork and other meats irradiated (12- to 90-kGy dose) at low temperatures (-15 to -45°C) show a lower thiamin loss after electron irradiation than after gamma irradiation. This is attributable to the DRE from the overlap of slowly diffusing spurs in the case of electron irradiation. A DRE is also evident in data on sprouting in potatoes and onions, indicating that electron irradiation inhibits sprouting more efficiently than gamma irradiation.

Many of the other nutrients analyzed, e.g., vitamin C in foods irradiated at low doses (<5 kGy),  $\alpha$ -tocopherol (vitamin E) in sunflower oil and amino acids in radappertized meats, show no such DRE.

Some minor differences between gamma and electron irradiation in the yields of volatile products can be identified in the available results. The yields in the case of electron irradiation, though apparently somewhat higher, are still very low (ppb to ppm;  $\mu\text{g}$  to mg/kg).

The sensory characteristics and consumer acceptance ratings show no significant differences between gamma- and electron-irradiated foods.

Overall, gamma and electron irradiation of foods appear to be equally effective.

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Whiteshell Laboratories  
Pinawa, Manitoba ROE 1LO  
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## CONTENTS

	<u>Page</u>
1. INTRODUCTION	1
2. BASIC ASPECTS OF DOSE RATE EFFECT	2
2.1 INITIATION OF RADIOLYTIC REACTIONS	2
2.2 DOSE RATE EFFECT	6
2.3 OXIDATION AND DOSE RATE EFFECT	10
2.4 SPUR OVERLAP AND DOSE RATE EFFECT	11
2.5 COMPUTER MODELLING	12
2.6 SUMMARY	13
3. IRRADIATORS AND DOSE RATES	14
4. DOSE RATE EFFECT ON FOODS: EXPERIMENTAL ASPECTS	14
4.1 MICRONUTRIENTS	14
4.1.1 Water-Soluble Vitamins	16
4.1.1.1 Thiamin (Vitamin B <sub>1</sub> )	16
4.1.1.2 Pyridoxine	22
4.1.1.3 Riboflavin (Vitamin B <sub>2</sub> )	22
4.1.1.4 Ascorbic Acid (Vitamin C)	23
4.1.1.5 Other Water-Soluble Vitamins	26
4.1.2 Lipid-Soluble Vitamins	26
4.1.2.1 Vitamin E	27
4.1.2.2 Other Fat-Soluble Vitamins	30
4.2 MACRONUTRIENTS	31
4.2.1 Amino Acids and Proteins	31
4.2.1.1 Amino Acids	32
4.2.1.2 Proteins	37
4.2.2 Carbohydrates	38
4.2.3 Lipids	41
4.3 VOLATILE COMPOUNDS	43
4.4 SPROUTING	45
5. SENSORY CHARACTERISTICS	47
6. CONCLUSIONS	52
ACKNOWLEDGEMENTS	54
REFERENCES	54
APPENDIX A SPUR OVERLAP: AN ESTIMATE	65
APPENDIX B RADIOLYTIC REACTIONS OF WATER	68

## 1. INTRODUCTION

Although most foods lose some vitamins and other nutrients during processing and storage, food is generally processed in a manner that minimizes nutrient loss and maximizes product safety. The nutrient content of food is also affected by preprocessing factors such as genetic variation, degree of maturity, soil conditions, use of fertilizer, climate and handling (Archer and Tannenbaum 1979). While radiation processing of foods can lead to some losses of the sensitive vitamins (e.g., thiamin, vitamin E), in general, food irradiation at the doses (<10 kGy) recommended by the Codex Alimentarius Commission (1983) causes no significant loss in nutritional quality (Tajuma et al. 1970, Taub et al. 1979a, 1979b, Graham 1980, Murray 1983).

It has been suggested (Hannah and Simic 1985, Raica et al. 1972, Skala et al. 1987, Thayer 1987, Thomas et al. 1981) that the observed minor losses of nutrients may even be decreased when foods are irradiated at high dose rates (electron beams from accelerators), rather than at the lower dose rates typical of gamma irradiation ( $^{60}\text{Co}$  or  $^{137}\text{Cs}$ ). The possible beneficial effect of higher dose rates has often been referred to as the "dose rate effect" (DRE). Brasch and Huber (1947) considered the ultrashort exposure times that are possible with highly accelerated electrons to be a vital factor in suppressing undesired side reactions in food irradiation. Studies of dilute solutions of organic compounds, e.g., phenol, glucose, linoleic acid, ascorbic acid and vitamin A-acetate, support the suggestions that there is lower loss of these compounds at higher dose rates (Dorfman et al. 1962, Mead 1952, Schuchmann and von Sonntag 1977, Simic 1983, Taimuty and de LaRue 1957). On the other hand, Taub et al. (1979a) concluded that, in general, such a DRE should not be expected from the irradiation of foods, since the first-order reactions of the primary species from water (hydroxyl radicals, hydrated electrons and hydrogen atoms) with the main components of foods (proteins, carbohydrates, etc.) will predominate. However, there seems to have been no comprehensive review of the relevant data on DRE in food irradiation. This is partly because of the paucity of data on the electron-beam irradiation of foods, which, until recently, was not considered practical.

The main objective of this review is to consider briefly the basic aspects of DRE and evaluate the available comparative data on the gamma and electron irradiation of foods. A particular aim is to determine whether any significant differences in the effects of irradiation of foods at different dose rates exist, based on known chemical and sensory effects. Although microbiology is not covered in this review, a few studies indicate only a minor DRE, if any, on microorganisms and insects (Adem et al. 1979, Hansen 1966, Shamsuzzaman, personal communication, Taimuty and de LaRue 1957, Tilton and Brower 1983, Weber 1983). One exception appears to be the DRE on adult Mexican fruit fly emergence where larvae were exposed to 10 Gy total dose at dose rates between 0.1 and 40 Gy/min (Lester and Wolfenbarger 1990).

## 2. BASIC ASPECTS OF DOSE RATE EFFECT<sup>1</sup>

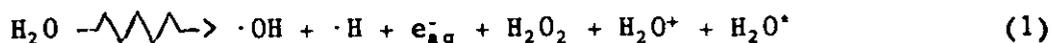
### 2.1 INITIATION OF RADIOLYTIC REACTIONS

The exposure of a substrate to ionizing radiation (radiolysis) results in the formation of a spectrum of ionized and excited species, which are either deactivated to the starting substrate or converted to other products, usually via free radicals (Draganic and Draganic 1971, Simic 1983, Singh and Singh 1982).

In radiolysis, the absorbed energy of a mixture is distributed approximately in proportion to the mass ratio of its constituents (Klots 1968). In a biological system, for example, the energies deposited in the organic (R'RH) part (direct effect) and in the water part (indirect effect) are ~25 and ~75% respectively. (In foods, the water content varies; for example, in meats it is ~75% in fresh beef but only ~50% in smoked bacon, while it may be as little as 15% in grains and as much as 80% in fruits (Singh 1989). Radiolysis leads to the formation of reactive intermediates in water (Reaction (1)) and organic components (Reaction (2)), as follows:

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<sup>1</sup>Prepared in consultation with A. Singh



The free radicals formed from the organic components (Reaction (2)) include those formed by the C-C (R'·) and the C-H (R'R·) bond breakages.

On the microscopic scale, energy deposited in the liquid and the solid phases is not distributed homogeneously but deposited in units of 20-100 eV in regions called spurs (Samuel and Magee 1953), about 5 nm in diameter (Mozumder 1969, Schwartz 1969). A typical spur, based on the parameters used by Schwartz (1969) to model radiolytic reactions in water, is shown in Figure 1. The spur consists of a spherical core, where the cationic and free radical species are formed, and an outer sphere defining the space within which the  $e_{\text{aq}}^-$  is formed. In liquid water, the resulting distribution of the major reactive species ( $\cdot\text{OH}$ ,  $\cdot\text{H}$  and  $e_{\text{aq}}^-$ ) is initially inhomogeneous at  $\sim 10^{-12}$  s after each energy deposition event, but becomes homogeneous by diffusion in  $\sim 10^{-7}$  s, as shown in Figure 2. The concentrations of the primary reactive species formed in spurs are quite high (Figures 1 and 2). For example, in water, the primary concentrations of hydrogen atoms ( $\cdot\text{H}$ ), hydroxyl radicals ( $\cdot\text{OH}$ ) and hydrated electrons ( $e_{\text{aq}}^-$ ) in spurs average  $\sim 10^{-2}$ ,  $\sim 10^{-1}$ , and  $\sim 10^{-1}$  mol·dm<sup>-3</sup> respectively, while in the spur core (central 0.75 nm), the initial concentrations of  $\cdot\text{H}$  and  $\cdot\text{OH}$  could be as high as  $\sim 0.5$  and  $\sim 2$  mol·dm<sup>-3</sup> (Figure 1) respectively (Singh and Singh 1982). Figure 2 is a qualitative representation of how spur formation in liquid water would appear if the radiolysis were done with a single gamma photon and a single electron. It is meant to indicate that the initial spur concentration would be much higher in the case of electron irradiation than in the case of gamma irradiation. This difference is due to much higher energy loss per unit volume of water from electron than from gamma irradiation (Klots 1968).

Diffusion during the first  $10^{-7}$  s reduces these concentrations in water at room temperature by many orders of magnitude, e.g., to  $\sim 10^9$  mol·dm<sup>-3</sup> for gamma irradiation and to  $10^{-3}$  to  $10^{-6}$  mol·dm<sup>-3</sup> for electron irradiation. This large difference in concentration in the steady-state homogeneous system of the reactive species formed on

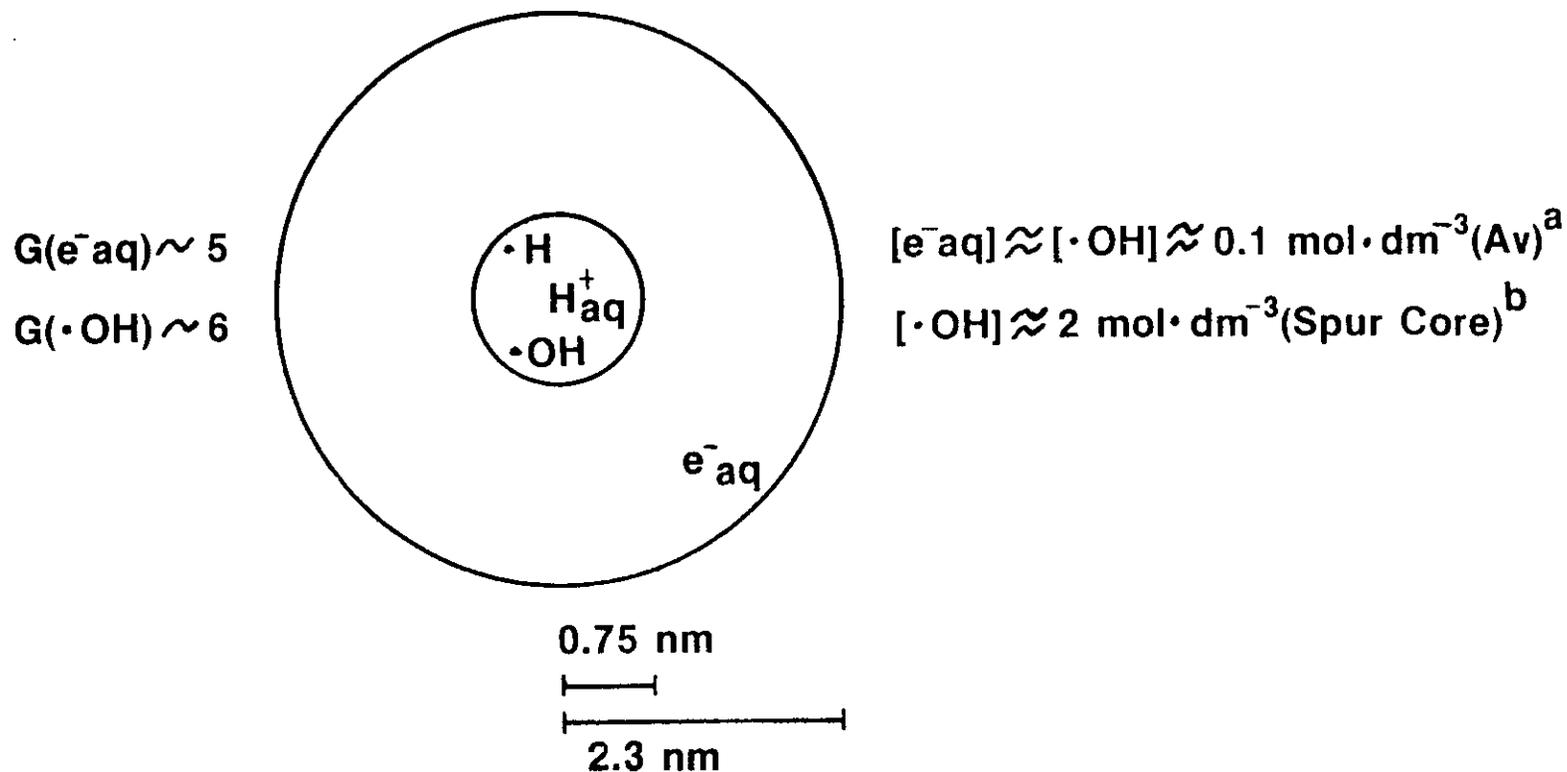


FIGURE 1: A Typical Spur in Water, Based on the Parameters Used by Schwartz (1969), Adapted from Singh and Singh (1982). The G-values given are based on the data of Jonah and Miller (1977) and Singh et al. (1978). Initial concentration: (a) averaged over total spur volume (diameter 4.6 nm); (b) within the spur core (diameter 1.5 nm).

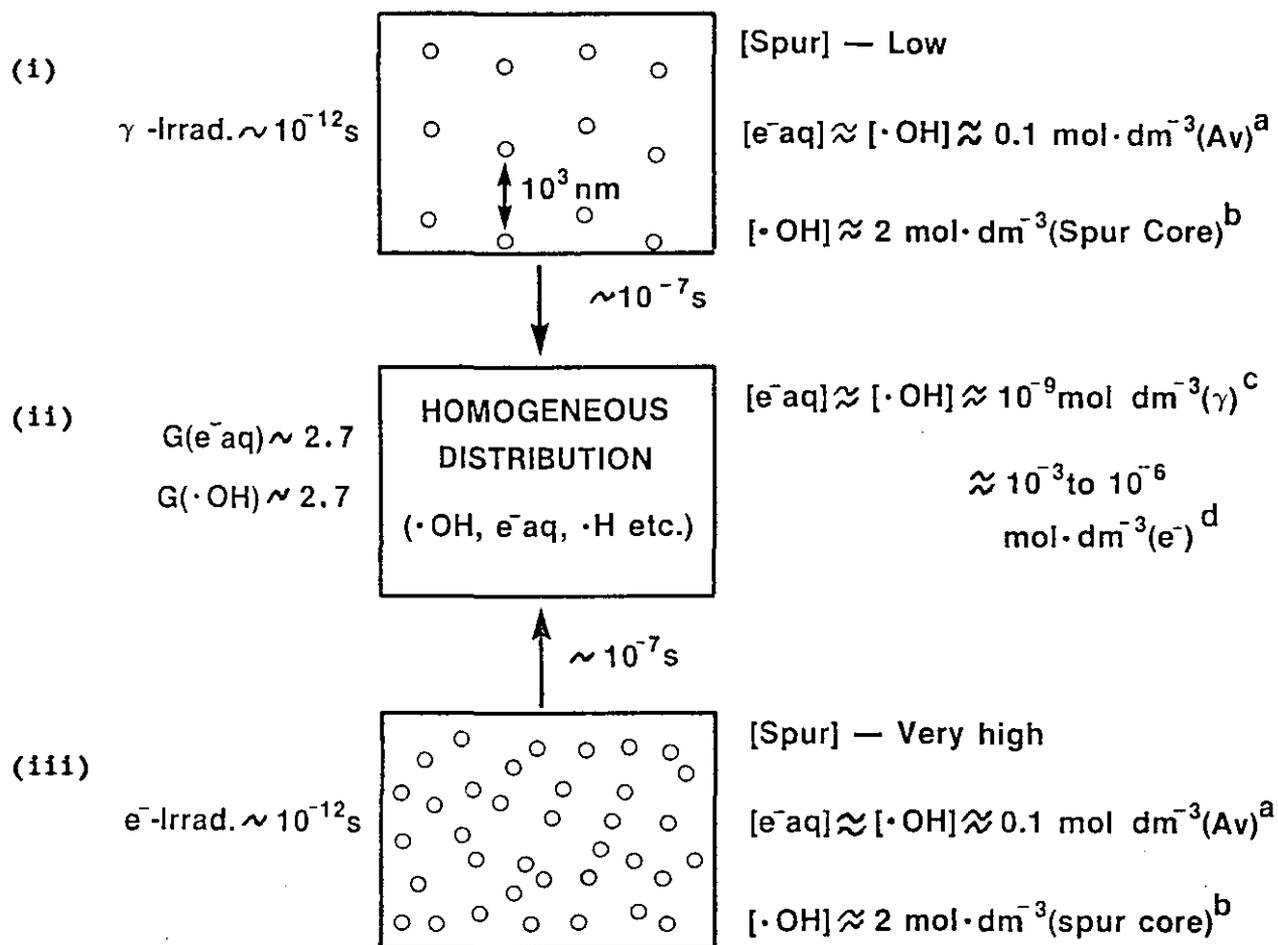
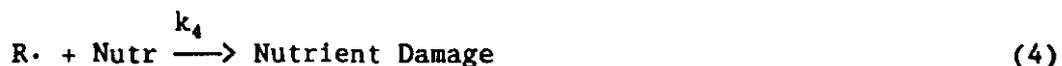


FIGURE 2: Transition from Inhomogeneous to Homogeneous Distribution of Free Radical Species in Liquid  $H_2O$ . (i) represents spur formation on energy absorption from a single gamma photon in  $10^{-12}$  s or less; (ii) shows homogeneous distribution of reactive species on diffusion of spurs in about  $10^{-7}$  s and (iii) represents spur formation on energy absorption from a single electron in  $10^{-12}$  s or less. The higher spur concentration [spur] on electron irradiation is not drawn to scale. (a) Averaged over total spur volume (diameter 4.6 nm); (b) initial concentration within the spur core (diameter 1.5 nm); (c)  $\gamma$  refers to gamma irradiation; (d)  $e^{-}$  refers to electron irradiation.

radiolysis is due to the large differences generally seen in dose rates between gamma and electron irradiation. However, the concentrations within the spurs are normally independent of dose rate, except at extremely high dose rates ( $>10^6$  Gy/s) where significant spur overlap may occur (see Section 2.4 and Appendix A).

## 2.2 DOSE RATE EFFECT

To illustrate the basis of the DRE, one may consider a general case where a radiolytically produced free radical, R·, reacts either with itself (recombination Reaction (3)) or with food components (e.g., nutrients, Nutr) to cause damage (damaging Reaction (4)).



The radical R· may be produced by direct or indirect effect. Two different cases can be considered: a dilute solution (one solute, e.g., Nutr  $\sim 10^{-5}$  mol·dm<sup>-3</sup>) and a food item (e.g., beef containing 75% water and 25% organic food components; [FC], 2.5 mol·dm<sup>-3</sup>, Table 1). Further, it is assumed that  $k_3 = 10^{10}$  mol<sup>-1</sup>·dm<sup>3</sup>·s<sup>-1</sup> and  $k_4 = 10^9$  mol<sup>-1</sup>·dm<sup>3</sup>·s<sup>-1</sup> for Reactions (3) and (4) respectively, based on the known rates of reactions of ·OH radicals (Buxton et al. 1988). The estimated relative importance of Reactions (3) and (4) based on these assumptions is shown in Table 1.

The importance of Reaction (3) increases by a factor of  $10^6$  going from gamma to electron irradiation, both for dilute solution and for beef. However, one important difference exists: in the case of the dilute solution, Reaction (3) occurs only about once for every 1000 times Reaction (4) occurs during gamma irradiation, while during electron irradiation Reaction (3) becomes dominant (at 1000 to 1). On the other hand, in the case of beef, Reaction (3) (compared with Reaction (4)) increases from an insignificant share of 4 in a billion in the case of gamma irradiation to a larger but still negligible share of 4 in 1000 in the case of electron irradiation. Thus the relative importance of Reaction (4) as compared with Reaction (3) decreases with increasing dose rate, mainly in dilute solutions.

TABLE 1  
RELATIVE IMPORTANCE OF RECOMBINATION REACTION (3) AND  
DAMAGING REACTION (4) ( $k_3 = 10^{10}$  and  $k_4 = 10^9 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$ )  
FOR THE SAME TOTAL DOSE<sup>1,2</sup>

System	Irradiator	Free Radical Concentration [·R] mol·dm <sup>-3</sup>	Food Component Concentration [FC] mol·dm <sup>-3</sup>	Relative Importance of Reactions (3) (4)
Dilute solution <sup>3</sup>	Gamma	10 <sup>-9</sup>	10 <sup>-5</sup>	1 : 10 <sup>3</sup>
Dilute solution <sup>3</sup>	Electron	10 <sup>-3</sup>	10 <sup>-5</sup>	1 : 10 <sup>-3</sup>
Beef	Gamma	10 <sup>-9</sup>	2.5	4 : 10 <sup>9</sup>
Beef	Electron	10 <sup>-3</sup>	2.5	4 : 10 <sup>3</sup>

1. Relative importance of Reaction (3)/Reaction (4) =  $\frac{k_3 [R \cdot]}{k_4 [FC]}$ .
2. It is assumed that beef behaves as an aqueous solution, since the relative values of  $k_3$  and  $k_4$  in beef are not known. The calculations are made for the systems at room temperature.
3. Water solution with only one solute.

In general, a similar DRE would be expected for all free radical species, whether primary or secondary, formed by direct or indirect action of radiation. The differences in the relative importance of the relevant analogues of Reactions (3) and (4) would depend on the relative reaction rates, and the complexities of the exact mechanisms of reactions. Where simple mechanisms analogous to Reactions (3) and (4) dominate, one would expect an observable DRE in dilute solutions but a negligible DRE in the case of foods, based on the data in Table 1.

This expectation is borne out in radiolysis studies of dilute aqueous solutions as shown by data on the gamma and electron radiolysis of solutions of vitamin A-acetate (Figure 3) and ascorbic acid (Figure 4), as reported by Taimuty and de LaRue (1957). In both cases, Taimuty and de LaRue (1957) observed a greater loss from gamma irradiation, for the same absorbed dose. Schuchmann and von Sonntag (1977), and Simic (1983)

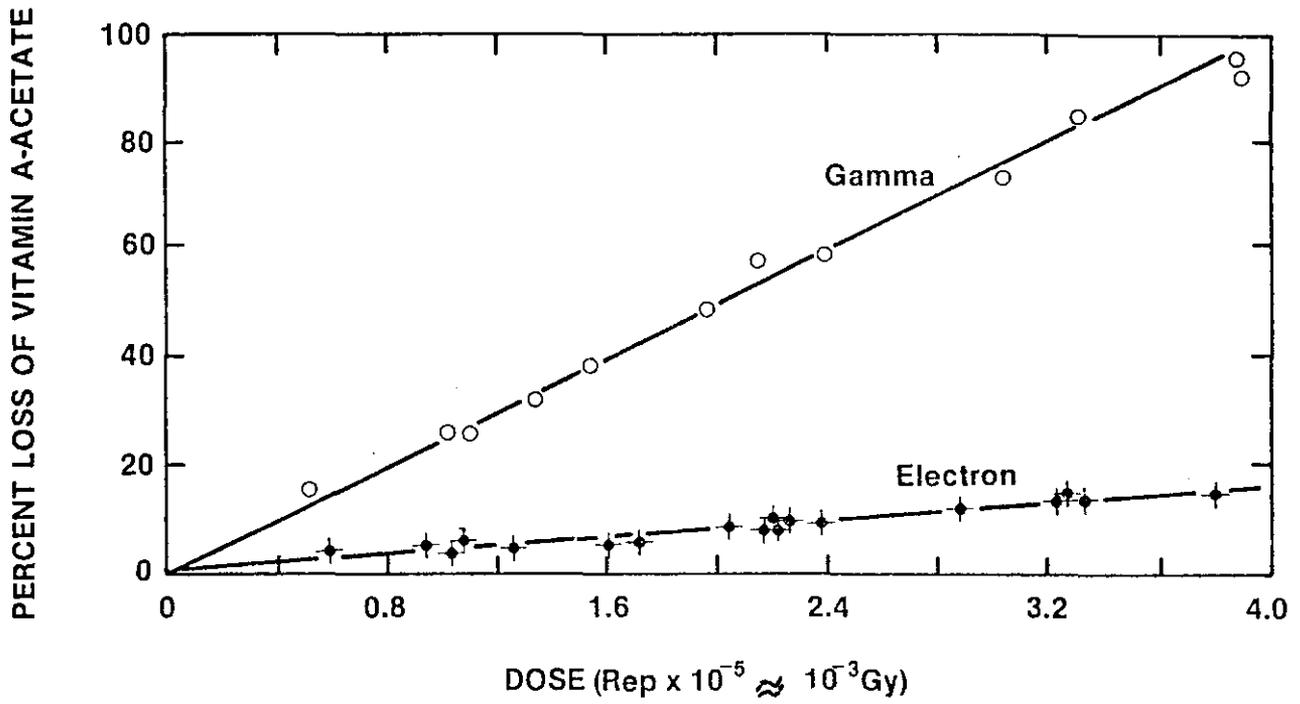


FIGURE 3: Loss of Vitamin A-Acetate in Isopropanol Solution from Gamma (Dose Rate ~ 10 Gy/s) and Electron (Dose Rate ~ 10<sup>4</sup> Gy/s) Irradiation. Data from Taimuty and de LaRue (1957).

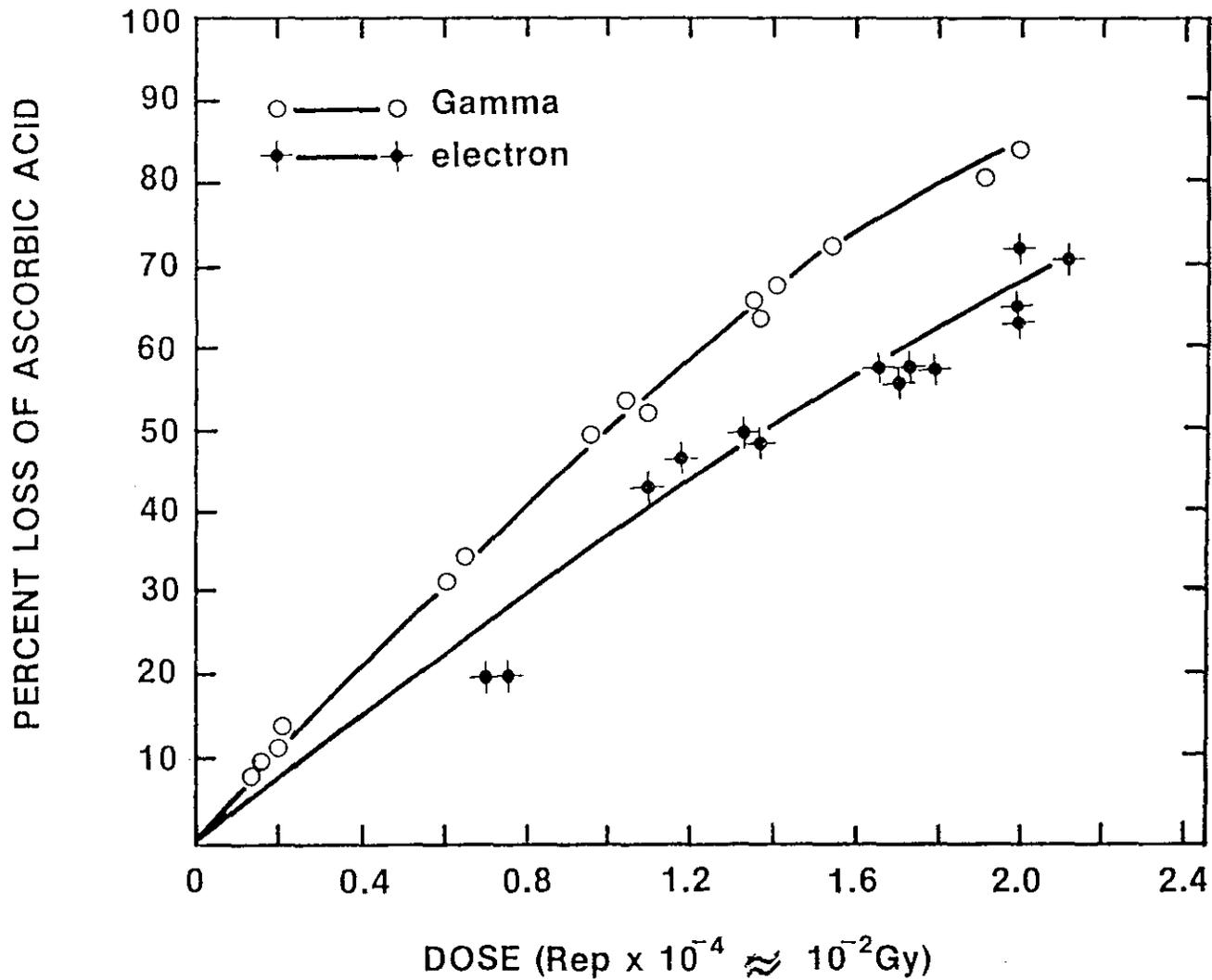


FIGURE 4: Loss of Ascorbic Acid in Aqueous Solution from Gamma (Dose Rate  $\sim 10$  Gy/s) and Electron (Dose Rate  $\sim 10^4$  Gy/s) Irradiation. Data from Taimuty and de LaRue (1957).

reported similar conclusions from work on glucose solutions. Mead (1952) also reported higher product yields at lower dose rates from the irradiation (using the Picker 250-KVP Therapy Tube) of linoleic acid (in 5% methanol) in buffered aqueous solution, pH 9.0, as shown in Table 2. The radiolytic products were not identified by the author. In this case, however, the free radical species reacting with linoleic acid would be the radicals derived from methanol by reaction with  $\cdot\text{OH}$  and  $\cdot\text{H}$  radicals, as follows:

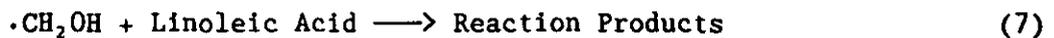


TABLE 2

DOSE RATE EFFECT ON PRODUCT FORMATION FROM LINOLEIC ACID<sup>1</sup>

Dose Rate <sup>2</sup> (Gy/min)	[Product] ( $10^{-5}$ mol.dm <sup>-3</sup> )
~0.10	28.2
~0.33	11.8
~0.98	5.0
~5.40	2.0

1. Data from Mead (1952). Irradiation temperature not given. Irradiation source, Picker-250 KVP Therapy Tube. Linoleic acid,  $5.8 \times 10^{-3}$  mol.dm<sup>-3</sup> in borate buffer, pH 9.
2. Given as r/min for a total dose of 1000 r (~10 Gy).

2.3 OXIDATION AND DOSE RATE EFFECT

In the presence of oxygen, organic free radicals may react with oxygen to form peroxy radicals:



This reaction would compete with the recombination reaction of the free radicals:



So, as the dose rate increases, the recombination reaction would be favoured over the peroxy radical formation. As a consequence, lower oxidation of food components may be expected from irradiation at higher dose rates. It appears, however, that no relevant work has been done to test this expectation.

#### 2.4 SPUR OVERLAP AND DOSE RATE EFFECT

As noted in Section 2.1, concentrations of free radical species within spurs do not change with dose rate, except at very high rates ( $>10^8$  Gy/s), where spur overlap becomes significant. In addition to the dose rate, spur overlap would also increase if spur lifetime increased, e.g., because of the low temperature of frozen systems.

The diffusion rates of reactive species in spurs depend on the viscosity of the system. Thus, the diffusion rate would be lower in solid foods (e.g., grain and frozen meats, for which spur diffusion rates do not seem to be available), which would decrease the DRE except where spur overlap occurred (see below). However, even in the solid phase, the DRE would still depend on the relative changes in the importance of Reactions (3) and (4) (and their analogues). Spur overlap would become important during electron irradiation of frozen samples (e.g., meats irradiated at  $-15$  to  $-40^\circ\text{C}$ ) at dose rates lower than those required in liquid  $\text{H}_2\text{O}$  for spur overlap; as the temperature was lowered, the diffusion rate of spurs (and hence of free radicals) would be dramatically reduced in frozen aqueous systems. Unfortunately, no estimates are available on spur diffusion rates in frozen systems (A. Mozumder, personal communication) and solids. It is not even certain whether homogeneous concentrations of free radicals could ever be reached in frozen systems (particularly in the case of meats at  $-15$  to  $-40^\circ\text{C}$ ). The overall effect of spur overlap in frozen systems would be to increase the DRE, owing to slow spur diffusion.

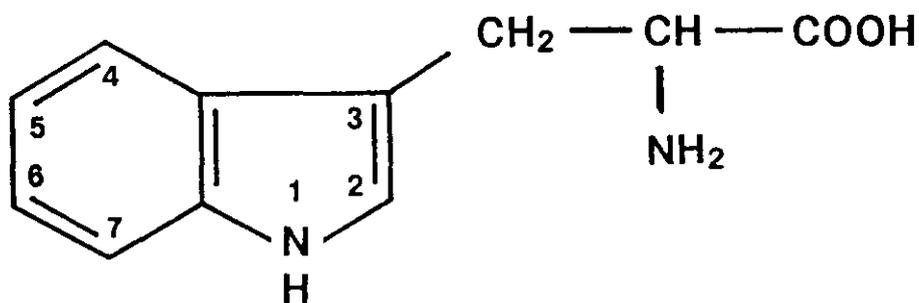
Since the rate and extent of spur diffusion would be much lower in solids, one would expect much less damage to nutrients in frozen foods ( $-30 \pm 10^\circ\text{C}$ ) than in foods at  $0$  to  $5^\circ\text{C}$ , for both gamma and electron irradiation. In the case of electron irradiation, DRE would also be a factor, owing to much greater spur overlap in the case of frozen meats. It should be pointed out that the total number of spurs formed, for the same total dose, would be the same for gamma and electron irradiation. The spur diffusion rate would be reduced in frozen solution and the consequent lifetime of the spur would be increased enough (e.g.,  $10^{-3}$  s instead of  $10^{-7}$  s in liquid  $\text{H}_2\text{O}$ ) to allow spur overlap during electron irradiation but not during gamma irradiation. Data supporting these expectations are discussed in Section 4.1.1.1 for thiamin.

It is relevant to point out that, at low temperatures ( $-30 \pm 10^\circ\text{C}$ ) or in solids at ambient temperature (e.g., grains), the spurs would still diffuse, though slowly. The diffusion rates of the three main reactive species (derived from water, for the sake of this discussion) in the above systems will roughly be inversely proportional to their molecular weight. Thus, H atoms would be the most mobile,  $e_{aq}^-$  less mobile and  $\cdot\text{OH}$  the least mobile. This would affect the DRE in foods at low temperatures. The mobility of  $e_{aq}^-$  would depend on its diffusion mechanism: if it acted as a hydrated species ( $e_{aq}^-$ ), it would diffuse most slowly. However, if it migrated from one hydration site to another, it would diffuse quickly (A. Singh, personal communication). Information on this subject is not readily available.

## 2.5 COMPUTER MODELLING

In principle, it should be possible to use computer modelling to calculate the expected differences in the effects of various dose rates if the mechanisms of the relevant radiolytic reactions are known. The number of radiolytic reactions that occur from the irradiation of a pure substrate, such as water, is large ( $\sim 50$ , Appendix B). This number increases rapidly with the number of components/solutes to  $>100$  for one-solute and to  $>1000$  for multisolute solutions.

A solution of tryptophan (I) may be taken as an example of water plus a one-component/solute system (Singh et al. 1984), to illustrate the increase in the number of reactive species, and hence in the reactions that occur as a solute is added to water.



I

In this case, the addition reaction of hydroxyl radicals can give up to six different free radicals (assuming the hydroxyl radical additions to be at carbons 2-7, in I above). The hydrogen atom abstraction reaction of hydroxyl radicals can give four more free radicals (assuming the abstraction of H from the CH<sub>2</sub>, CH and NH<sub>2</sub> groups from the side chain and of the NH group from the ring structure, in I above). Additional free radicals would also be expected from reactions of hydrated electrons and hydrogen atoms with tryptophan (Armstrong and Swallow 1969).

Most foods are multicomponent systems and thus the expected number of radiolytic reactions in a food is very large (>>100). Since all the possible reactions have yet to be identified and their rate constants established, it is impossible to model the reactions by computer to predict the expected DRE. The only practical alternative is to review the available relevant experimental data to identify any significant DRE.

## 2.6 SUMMARY

The existence of DRE in a system should depend on the following factors:

- (1) the rate constants for the analogues of Reactions (3) and (4) for each of the reactive free radical species;
- (2) the concentrations of various reactive food components in the system; and
- (3) the viscosity of the system.

The above factors should apply to a simple mechanism involving analogues of Reactions (3) and (4). Food systems are too complex to allow a prediction of the extent of DRE in a particular system on the basis of fundamental principles.

### 3. IRRADIATORS AND DOSE RATES

Although gamma irradiators ( $^{60}\text{Co}$  and  $^{137}\text{Cs}$  sources) have been the most common sources of food irradiation, electron-beam irradiators, particularly 5-MeV X-ray sources and 10-MeV electron accelerators, are becoming increasingly important. Characteristics of typical irradiators are given in Table 3, along with their dose rates, where available.

### 4. DOSE RATE EFFECT ON FOODS: EXPERIMENTAL ASPECTS

#### 4.1 MICRONUTRIENTS

Vitamins are an important group of micronutrients present in foods and are affected by processing conditions (Archer and Tannenbaum 1979, Erdman and Klein 1982, Osborne and Voogt 1978, Sauberlich et al. 1982). Their concentrations are generally small ( $\mu\text{g/g}$ ), a notable exception being vitamin C ( $\text{mg/g}$ ). They are usually subdivided into water- and fat-soluble vitamins. Their physical environment (water or lipids) determines the types of free radical reactions they undergo on irradiation

(Delincee 1983; Nawar 1983; Simic 1983; Singh 1987, 1988; Taub 1983). Fat-soluble vitamins are exposed mainly to radicals produced in the lipid phase (Nawar 1983), while water-soluble vitamins are primarily the targets of free radicals produced from water (Simic 1983).

TABLE 3  
TYPICAL IRRADIATORS AND THEIR DOSE RATES<sup>1</sup>

Type of Irradiator	Beam Voltage Range (MeV)	Electron-Beam Current Range (mA)	Dose Rate	
			Instantaneous Pulse (Gy·s <sup>-1</sup> )	Average (Gy·s <sup>-1</sup> )
Van de Graaff (High Voltage Engineering Corp.)	≤2	≤1.0		~2.5 x 10 <sup>4</sup>
Low-frequency capacitatively coupled (Nissin High Voltage)	0.5 to 3.0	≤30		~7.6 x 10 <sup>5</sup>
High-frequency capacitatively coupled, DC mode (Radiation Dynamics Inc.)	0.4 to 4.5	35 to 100		~8.9 x 10 <sup>5</sup> to 25 x 10 <sup>5</sup>
Low-frequency magnetically coupled (High Voltage Engineering Corp.)	0.3 to 3.0	25 to 100		~8.9 x 10 <sup>5</sup> to 25 x 10 <sup>5</sup>
I-10/1 (AECL)	10		~1.5 x 10 <sup>6</sup>	~1.8 x 10 <sup>3</sup>
I-10/50 (AECL)	10		~1.5 x 10 <sup>6</sup>	~9 x 10 <sup>4</sup>
NRC, LINAC	45		1.0 x 10 <sup>8</sup>	
Febetron 705	1.7		1.3 x 10 <sup>13</sup>	2.1 x 10 <sup>4</sup>
Febetron 706	0.6		1.3 x 10 <sup>13</sup>	2.1 x 10 <sup>3</sup>
Gammacell 220	1.17, 1.33			4
Carrier irradiator <sup>2</sup>	1.17, 1.33			~6

1. Information prepared with the help of Dr. J. Barnard. Some information from Saunders (1988).
2. Such as the one at Canadian Irradiation Centre, Laval, PQ, with an initial dose rate of ~5.5 Gy·s<sup>-1</sup>.

#### 4.1.1 Water-Soluble Vitamins

Water-soluble vitamins, such as B<sub>1</sub> (thiamin) and C (ascorbic acid), are the most sensitive to radiation (Day et al. 1957, Kraybill 1982, Wilson 1959, Ziporin et al. 1957, Wilska-Jeszka and Krakowiak 1975). A DRE on these vitamins in solutions is expected, based on studies of various organic compounds in solution by Hannan (1955), Kent et al. (1968), Schuchmann and von Sonntag (1977), Taimuty and de LaRue (1957) and Taub et al. (1979a). However, comparative work on DRE on vitamins in dilute solutions or in foods is limited.

##### 4.1.1.1 Thiamin (Vitamin B<sub>1</sub>)

Thiamin is distributed widely throughout plant and animal tissues, e.g., ~2 and ~2.8 mg/g in wheat germ and liver respectively, but much less widely in meat muscle, e.g., ~8 µg/g in pork muscle and ~1 µg/g in muscle of other animal species (Simic 1983). Thiamin deficiency causes the well-known disorder beriberi. Thiamin is not very stable and is readily destroyed when treated by heat or chemicals (sulfite, nitrite). Thermal destruction gives a characteristic odour, which contributes to the "meaty" flavor in cooked meats (Simic 1983, Pennema 1985).

Diehl (1975) found no specific DRE on the loss of thiamin in solution (Table 4) in a narrow range (given as 10<sup>7</sup> to 10<sup>8</sup> Gy/s during the pulse or 12.5 to 125 Gy/s as the average dose rate for the scanning electron beam), using electrons from a 10-MeV linear accelerator. Irradiations were carried out at 0°C, with a total radiation dose of 0.5 kGy. The absence of a DRE in this case could be due to the very small difference between the two dose rates used. A more recent study (Chuaqui-Offermanns, personal communication), using a somewhat wider difference between dose rates (~10<sup>6</sup> Gy/s and ~3.6 Gy/s), indicates a slightly lower loss in the case of the high dose rate in dilute thiamin solutions (2 x 10<sup>-5</sup> mol·dm<sup>-3</sup>; ~0°C, samples kept on ice), with a total dose up to 3 kGy.

TABLE 4

DOSE RATE EFFECT ON THIAMIN IN SOLUTION<sup>1</sup>

Current (mA) <sup>2</sup>	40	80	200	400
Average Pulse Dose Rate (Gy/s)	10 <sup>7</sup>	2 x 10 <sup>7</sup>	5 x 10 <sup>7</sup>	10 <sup>8</sup>
Average Scanning Beam Dose Rate (Gy/s)	12.5	25.0	62.5	125.0
Duration of Irradiation (s)	40	20	8	4
Percent Loss of Thiamin	51.2	48.8	47.2	53.0

1. Data from Diehl 1975.
2. 10-MeV linear electron accelerator; irradiations of 1 mg/mL thiamin dichloride solutions at 0°C, total dose 0.5 kGy.

However, in the case of high-dose irradiation of meats, data exist that indicate only a minor DRE on thiamin destruction from irradiation above freezing temperatures. Raica et al. (1972) reported that, although the destruction of thiamin in meats containing relatively high levels of the vitamin was slightly greater, irradiation to doses between 20 and 60 kGy at 0 to 5°C resulted in no significant difference (<10%) in its retention as a function of dose rate, as shown in Figure 5.

On the other hand, data reported by Thomas et al. (1981) on the radappertization (radiation sterilization) of pork at very low temperatures (frozen samples) show a very high retention of thiamin at high dose rates. The data in Figure 6 show that thiamin loss is lower at lower temperatures and higher dose rates (electron irradiation), thus establishing DRE clearly. As explained earlier, this is attributable to spur overlap from low-temperature electron irradiation.

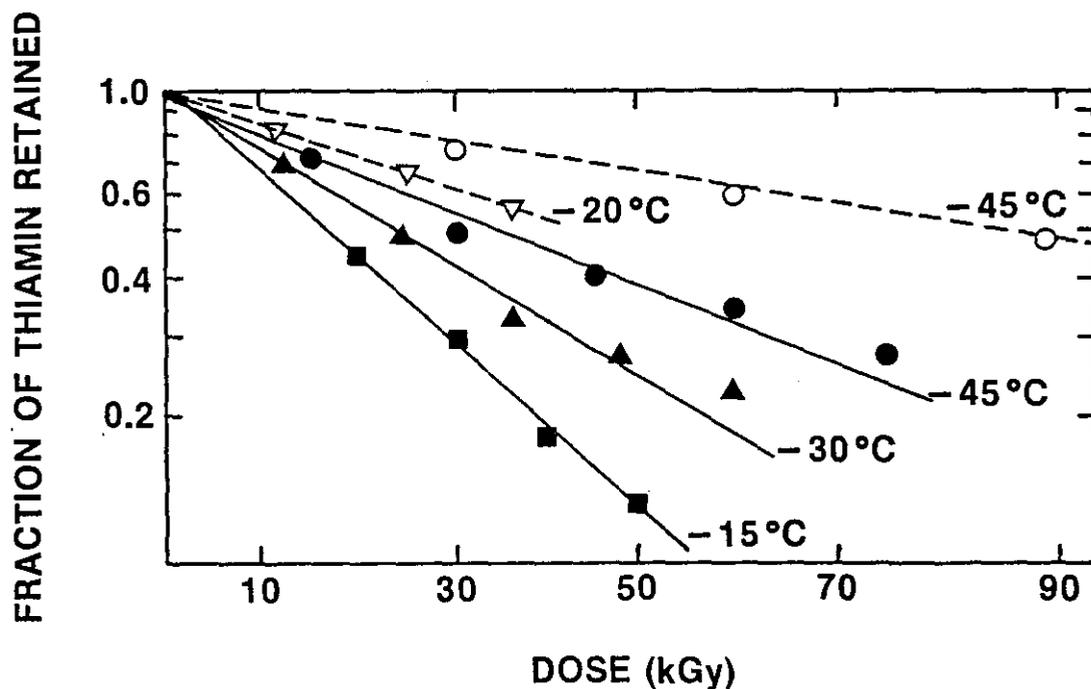


FIGURE 6: Effect of Dose Rate and Temperature on Thiamin. Data from Thomas et al. (1981). Initial thiamin concentration about 9  $\mu\text{g/g}$  in pork. Interrupted lines (---), 10-MeV linear electron accelerator irradiation; solid lines (—), gamma irradiation. Dose rates not given in the paper but, based on Shults and Wierbicki (1980), assumed to be  $\sim 14$  Gy/s for gamma and  $\sim 10^6$  Gy/s for electron irradiation.

Skala et al. (1987) and McGown et al. (1979a) have reported results on frozen radappertized beef and chicken irradiated at  $-30 \pm 10^\circ\text{C}$ , which also suggest better thiamin retention in electron-irradiated samples than in gamma-irradiated samples (Table 5). These results are consistent with the trend seen in pork irradiation at very low temperatures ( $-15$  to  $-45^\circ\text{C}$ , Thomas et al. 1981, Figure 6) and in chicken irradiation ( $-25 \pm 15^\circ\text{C}$ , Thayer 1990, Table 5). The reasons for the difference in degree of thiamin retention in chicken (Table 5) between the results reported by Skala et al. (1987) and those reported by Thayer (1990) are not clear but may be related to different thiamin detection methods; while Thayer (1990) used a chemical method, Skala et al. (1987) used a microbiological assay.

TABLE 5  
DOSE RATE EFFECT ON VITAMINS IN MEATS

Vitamin	System	Average Total Dose (kGy)	Irradiation (at $-30 \pm 10^\circ\text{C}$ )		Reference
			Gamma	Electron	
			Percent Retention		
Thiamin	Beef	58 <sup>1</sup>	23	44	Skala et al. (1987), McGown et al. (1979)
	Chicken	58 <sup>1</sup>	26	66	Skala et al. (1987)
	Chicken	45-68 <sup>2</sup>	~68	-86	Thayer (1990)
Pyridoxine	Chicken	58 <sup>1</sup>	50	62	Skala et al. (1987)
	Chicken	45-68 <sup>2</sup>	73	93	Thayer (1990)

1. Gamma and electron dose rates not given but assumed to be  $-14$  Gy/s and  $-10^6$  Gy/s respectively, based on data from Shults and Wierbicki (1980).
2. Gamma and electron dose rates  $9.6$  and  $-10^6$  Gy/s respectively (Thayer, personal communication).

Limited data are available from which to compare the DRE at doses <10 kGy on thiamin retention in foods. Thayer and his co-workers (Fox et al. 1989, Jenkins et al. 1989) have undertaken extensive work on the effect of low-dose irradiation, storage and cooking on the content of thiamin and other water-soluble vitamins (riboflavin, pyridoxine, niacin, etc.) in pork and other meats. Jenkins et al. (1989) calculated a loss of 11.2% for thiamin in gamma-irradiated pork at a dose of 1 kGy (dose rate ~2.1 Gy/s) at 0°C. In comparing their result with the 5% loss of thiamin observed by Diehl (1975) from electron irradiation using a 10-MeV linear accelerator (dose rate 12.5 Gy/s for a 1-kGy dose), Jenkins et al. (1989) postulated that the difference might be due to DRE. However, as discussed earlier in this section, Raica et al. (1972) observed no significant DRE, even at higher doses (≥20 kGy), in their work on several meats irradiated at 0-5°C.

Though sweet potatoes have low thiamin levels (0.018 µg/g), Lu et al. (1989) saw no DRE on their thiamin content (Table 6). Note that in this study the dose rate varied over a rather small range (0.27 to 3.75 Gy/s) and the sweet potatoes were irradiated at 24°C for periods varying from ~4 to 60 min (Table 6). In the case of orange juice, preliminary results show no significant DRE (Chuaqui-Offermanns, personal communication).

TABLE 6  
DOSE RATE EFFECT ON VITAMINS IN SWEET POTATOES<sup>1</sup>

Dose Rate (Gy/s)	Time of Irrad. <sup>2</sup> (min)	Thiamin	Riboflavin	Ascorbic Acid	Carotenoids
		mg/100 g (fresh weight) <sup>3</sup>			
3.75	4.4	0.016 <sup>a</sup>	0.036 <sup>a</sup>	16.43 <sup>abc</sup>	11.4 <sup>ab</sup>
2.88	5.7	0.015 <sup>a</sup>	0.036 <sup>a</sup>	16.34 <sup>abc</sup>	12.8 <sup>a</sup>
2.06	8.0	0.017 <sup>a</sup>	0.03 <sup>a</sup>	16.93 <sup>ab</sup>	7.7 <sup>c</sup>
1.37	12.1	0.016 <sup>a</sup>	0.04 <sup>a</sup>	15.05 <sup>c</sup>	8.6 <sup>bc</sup>
0.27	60.0	0.017 <sup>a</sup>	0.04 <sup>a</sup>	14.65 <sup>c</sup>	7.6 <sup>c</sup>
0	-	0.018 <sup>a</sup>	0.026 <sup>a</sup>	17.30 <sup>a</sup>	12.6 <sup>a</sup>

1. Data from Lu et al. (1989).
2. Time of irradiation (<sup>60</sup>Co source) at 24°C for a total dose of 1 kGy.
3. Mean values with the same superscripts (a, b, c) in the same column are not significantly different at the 5% level.

It would therefore be worthwhile to repeat some of this work to obtain a clearer picture of DRE in the case of low doses of irradiation, at 0 to 5°C, using a much wider range of dose rates, especially for meats.

#### 4.1.1.2 Pyridoxine

Pyridoxine is a member of the vitamin B<sub>6</sub> group widely distributed in living systems and an essential growth factor. It is present in meats at a concentration of 1 to 5 µg/g. Pyridoxine is frequently added to processed foods (Archer and Tannenbaum 1979, Fennema 1985).

In radappertized frozen chicken, the trend of DRE for pyridoxine levels is similar to that for thiamin, except that damage from both gamma and electron irradiation is less extensive (Table 5, Skala et al. 1987, Thayer 1990). The reason for the differences in the percentage retention of pyridoxine (Table 5) in the work of Skala et al. (1987) and Thayer (1990) is not clear. Both used a microbiological assay for pyridoxine. There appear to be no data in the literature from which to compare DRE at low doses (≤10 kGy) on pyridoxine content in foods.

#### 4.1.1.3 Riboflavin (Vitamin B<sub>2</sub>)

Riboflavin is not as radiation-sensitive as thiamin or pyridoxine. Day et al. (1957) reported that riboflavin in beef is fairly resistant to irradiation, since only 8% was destroyed by the irradiation process at a dose of 30 kGy. Heat processing of beef apparently has a greater destructive effect on riboflavin than radiation processing at either 28 or 56 kGy (Kraybill 1982). Taimuty and de LaRue (1957) could not observe a DRE (10<sup>3</sup> and 10<sup>6</sup> rep/s, ~10 and 10<sup>4</sup> Gy/s) on riboflavin in solution, contrary to the general observation of a DRE on other systems in dilute solutions, mentioned earlier in Section 2.2.

At low doses (1 kGy), Lu et al. (1989) reported no DRE on riboflavin content between 0.27 and 3.75 Gy/s in sweet potato tubers (Table 6). In the case of radappertized chicken (Table 7), Thayer (1990) observed no inactivation of riboflavin at high doses. In fact, the levels of riboflavin in both gamma- and electron-irradiated chicken were slightly higher than those in the unirradiated control, showing no significant DRE.

In their study of DRE, Taimuty and de LaRue (1957) reported reduced destruction of ascorbic acid (1% solution) at higher dose rates (Figure 4). Work on the retention of ascorbic acid in foods as a function of dose rate has been limited to low-dose irradiations. Somogyi et al. (1975) studied such effects on two varieties of potatoes (Maritta and Bintje) using 3-MeV electron (dose rate not given but expected to be  $\sim 10^6$  Gy/s) and gamma (5.5 and 6.3 kGy/h for Bintje and Maritta variety respectively) irradiation, up to a total dose of 1.5 kGy (Figure 7). They observed no significant DRE on the level of ascorbic acid in either variety. It should be mentioned here that the levels of ascorbic acid reported in this study ( $\sim 85$  mg/100 g) are much higher than those generally reported for potatoes (about 20 mg/100 g, Bowes et al. 1975). The authors do not comment on this difference.

Similarly, Umeda et al. (1970) observed no DRE on citrus fruit sections irradiated with a 1- to 5-kGy total dose (Table 8), using electron (1 MeV at  $0.4 \mu\text{A}/\text{cm}^2$ , dose rate not given but expected to be  $4.8 \times 10^4$  Gy/h) and gamma (dose rate 0.6 to 2.3 kGy/h) irradiation. In fact, they reported no significant loss of ascorbic acid, even at doses as high as 5 kGy. A recent study (Lu et al. 1989) reported a slightly higher retention of ascorbic acid at higher dose rates in sweet potatoes (Table 6). Since the irradiation times (for a total dose of 1 kGy) ranged from 3.9 to 60 min at  $24^\circ\text{C}$  using a  $^{60}\text{Co}$  source (Table 6), the possibility of ascorbate loss at this temperature during long periods of irradiation was raised by the authors. In view of these contradictory results, it would be useful to optimize the irradiation temperature, which is likely to be lower than  $24^\circ\text{C}$ .

In an earlier study, Lu et al. (1987) found no DRE on the ascorbic acid content of onions irradiated with a 2-MeV electron source (dose rate not given) and a gamma source (dose rate 0.38 Gy/s) up to a total dose ranging between 0.1 and 3 kGy.

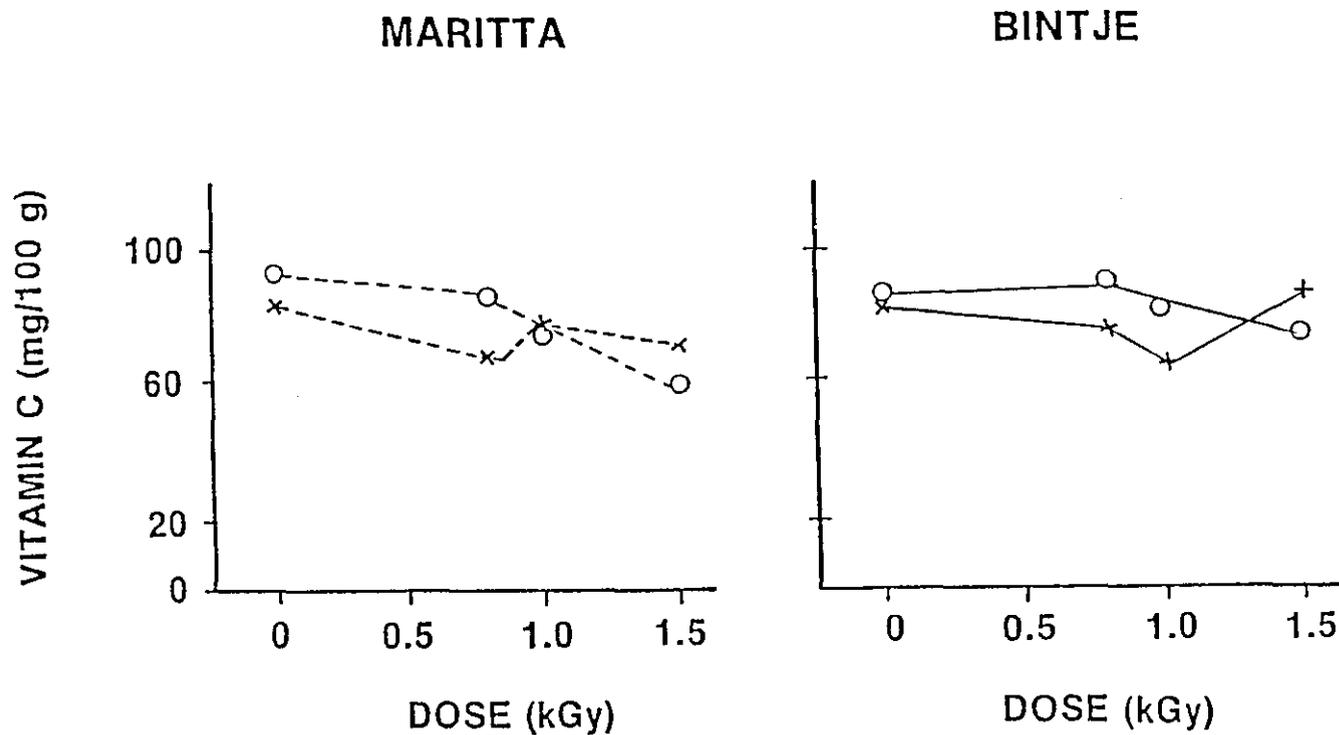


FIGURE 7: Effect of Gamma and Electron Irradiation on the Content of Vitamin C (Ascorbic Acid) in Two Varieties of Potatoes. Data from Somogyi et al. (1975). X = electron (3-MeV) irradiation (dose rate not given but assumed to be  $\sim 10^6$  Gy/s); o = gamma irradiation (6.3 kGy/h for Maritta and 5.5 kGy/h for Bintje variety).

**TABLE 8**

**EFFECT OF GAMMA AND ELECTRON IRRADIATION ON ASCORBIC ACID  
(VITAMIN C) CONTENT OF CITRUS FRUIT SECTION<sup>1</sup>**

Treatment	Ascorbic Acid Content (mg per fruit section)			
	Dose (kGy)			
	1	2	3	5
Unirradiated (control)	16.6	21.2	18.9	18.6
Electron irradiation (1 MeV, 0.4 $\mu$ A/cm <sup>2</sup> )	17.0	22.5	18.9	17.9
Gamma irradiation (0.6-2.3 kGy/h)	17.2	21.2	18.6	17.2

1. Data from Umeda et al. (1970). All fruit sections assumed to be of equal weight.

4.1.1.5 Other Water-Soluble Vitamins

Thayer (1990) has reported on the DRE on several other water-soluble vitamins in radappertized chicken (Table 7). The retention values for all the vitamins except choline and niacin (bound) are slightly higher in the case of electron irradiation than in the case of gamma irradiation. Incidentally, many of the values for irradiated chicken are higher than those for the unirradiated controls. While the reason for this is not clear, one possibility may be that relevant enzymes are activated on irradiation.

4.1.2 Lipid-Soluble Vitamins

Vitamin E, the most sensitive of the fat-soluble vitamins, is easily degraded by irradiation. The sensitivity of the fat-soluble vitamins follows the order: vitamin E > carotene > vitamin A > vitamin D > vitamin K (Kraybill 1982).

#### 4.1.2.1 Vitamin E

This fat-soluble vitamin is found in nature in the form of tocopherols and tocotrienols. While vitamin E has multiple physiological functions, its exact biochemical role remains to be defined (Tannenbaum et al. 1985). Its activity is widely distributed among food groups of animal and vegetable origin, including oils (Davis 1972, Slover 1971). The most active form of vitamin E is  $\alpha$ -tocopherol (Fennema 1985). The levels of  $\alpha$ -tocopherol in different foods (Machlin 1980, Sebrell and Harris 1972) range from 1 to 15  $\mu\text{g/g}$  in grains (Herting and Drury 1969), from 0.15 to 3  $\mu\text{g/g}$  in meats, poultry and fish (Ames 1972), and from 0.2 to 0.8  $\text{mg/g}$  in margarine and sunflower oil (Diehl 1970).

Although  $\alpha$ -tocopherol in solution is very sensitive to irradiation, solutions are not affected by different irradiation dose rates. Diehl (1979a) irradiated  $\alpha$ -tocopherol solution in isooctane, under nitrogen, with gamma radiation (1.8 Gy/s) and electrons ( $10^7$  Gy/s) and found identical pattern of destruction, as shown in Figure 8. Although the author does not mention the temperature during irradiation, his other published work refers to the irradiation of similar systems at 20°C (Diehl 1979b, Diehl and Kim 1981). Earlier, Diehl (1970) showed that, although  $\alpha$ -tocopherol loss was prevented to some extent by the exclusion of oxygen (nitrogen vs. air, Figure 9), there was no significant difference between its degradation in air and in nitrogen at dose rates between  $10^3$  and  $10^5$  Gy/s. Similar results were obtained with  $\alpha$ -tocopherol acetate in isooctane solution (Diehl 1970), but this compound was found to be less sensitive than  $\alpha$ -tocopherol to irradiation.

There have been only a few studies of DRE on  $\alpha$ -tocopherol content in foods. One such study (Diehl 1979a) used four different radiation sources: 1-MeV Van de Graaff accelerator,  $2.5 \times 10^4$  Gy/s; 10-MeV linear electron accelerator,  $10^7$  Gy/s; 5-mA X-ray, 4 Gy/s; and  $^{60}\text{Co}$ , 1.8 Gy/s. No significant differences were observed in  $\alpha$ -tocopherol loss from the irradiation of sunflower oil at a total dose of 1 kGy at the four different dose rates (Table 9). Samples under nitrogen lost slightly less

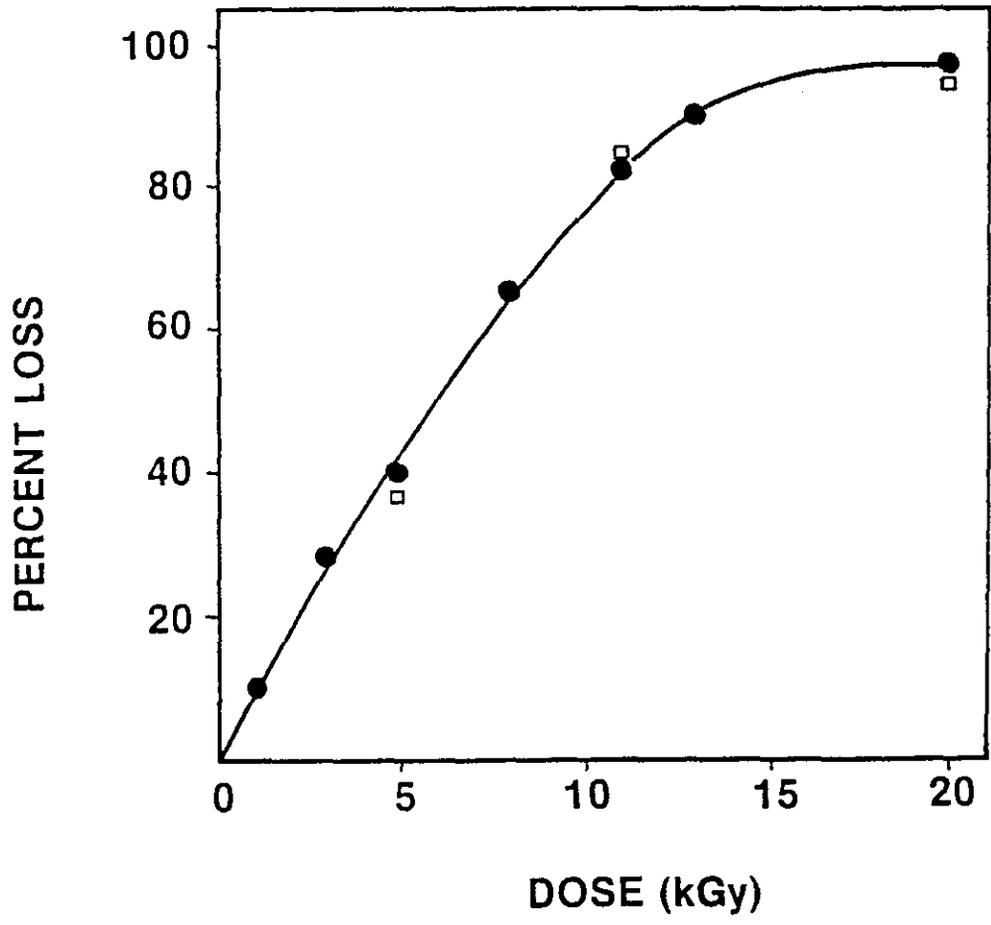


FIGURE 8: Dose Rate Effect on  $\alpha$ -Tocopherol in 0.1% Solution in Isooctane, Under Nitrogen. Data from Diehl (1979a). ● — ●, gamma irradiation (1.8 Gy/s); □ — □, electron irradiation (10-MeV linear electron accelerator,  $10^7$  Gy/s).

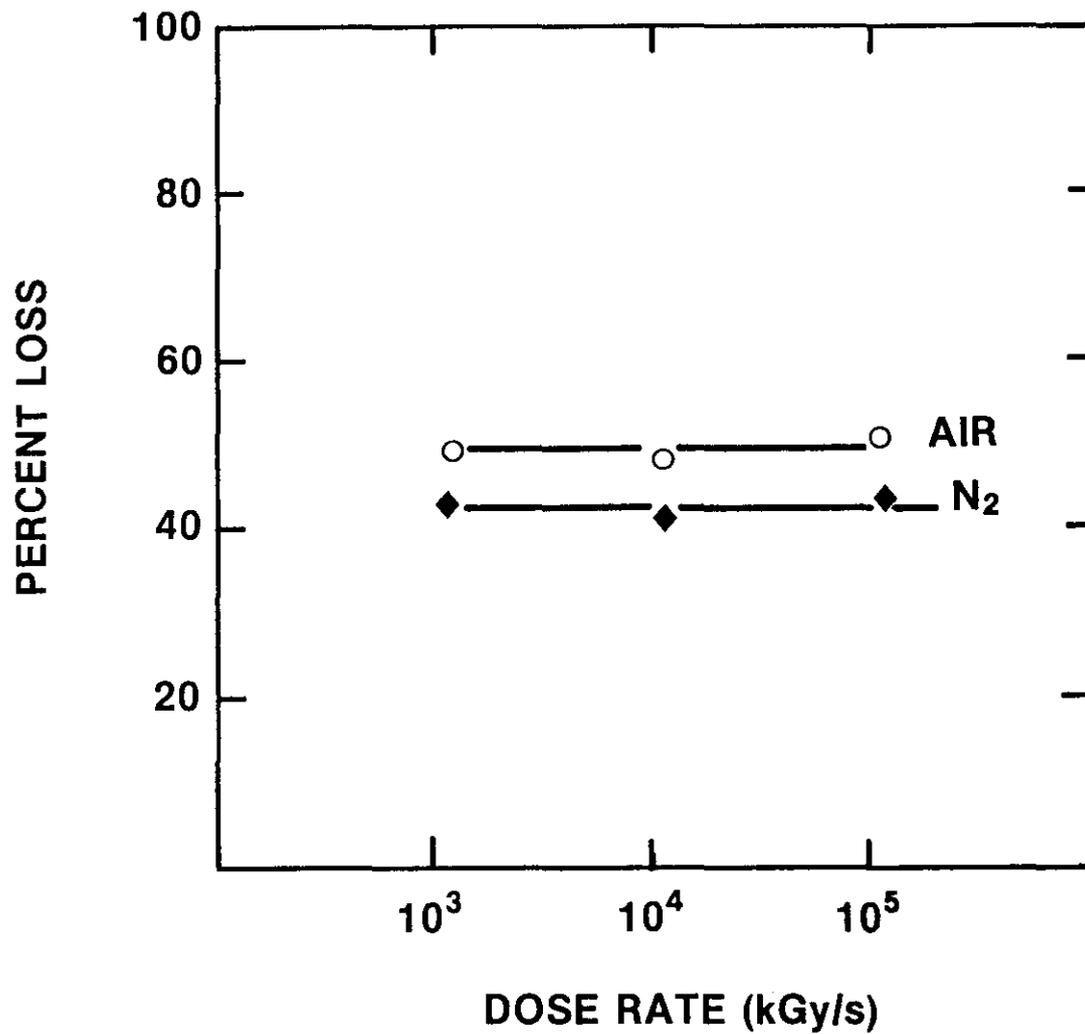


FIGURE 9: Electron Irradiation of  $\alpha$ -Tocopherol in Solution in Isooctane, Under Air and Nitrogen. Data from Diehl (1970). Total dose of irradiation (10-MeV linear electron accelerator) was 1 kGy.

TABLE 9

DOSE RATE EFFECT ON  $\alpha$ -TOCOPHEROL IN SUNFLOWER OIL<sup>1</sup>

Radiation Source	Dose (kGy)	Dose Rate (Gy/s)	Tocopherol Loss (%)	
			in Nitrogen	in Air
<sup>60</sup> Co	1	1.8	30.1	36.5
	10	1.8	89.4	94.6
X-ray (5 mA) (20 mA)	1	4	30.1 ± 1.0	34.8 ± 0.6
	10	16	86.0 ± 1.3	90.7 ± 1.2
Van de Graaff (1 MeV)	1	2.5 × 10 <sup>4</sup>	27.8 ± 0.4	33.5 ± 0.3
	10	2.5 × 10 <sup>4</sup>	91.1 ± 1.4	95.9 ± 0.5
Linear accelerator (10 MeV)	1	10 <sup>7</sup>	27.0	32.2

1. Data from Diehl (1979a).

$\alpha$ -tocopherol than those under air (Table 9). Similar results for DRE were obtained when sunflower oil samples were irradiated at a total dose of 10 kGy (Table 9), although the loss of  $\alpha$ -tocopherol was greater, as would be expected (Diehl 1979a). Diehl (1979a) concludes that the slight apparent trend (Table 9) in loss of  $\alpha$ -tocopherol at low dose rates (e.g., 1.8 and 4 Gy/s) of 30.1% vs. high dose rates (e.g., 2.5 × 10<sup>4</sup> and 10<sup>7</sup> Gy/s) of ~27% with a 1-kGy dose is not significant, especially since the same trend dose not exist for the 10-kGy dose.

#### 4.1.2.2 Other Fat-Soluble Vitamins

Most other fat-soluble vitamins are less sensitive to radiation than is vitamin E. Little work has been done on these vitamins, especially on the DRE, either in solution or in foods. In a study of DRE, Taimuty and de LaRue (1957) reported greater destruction of solubilized retinyl acetate (vitamin A derivative) in isopropanol by gamma than by electron irradiation (Figure 4). However, no DRE on vitamin A was observed in radappertized chicken (Thayer 1990, Table 10). Thayer (1990) also reported data on DRE on vitamins D, K and B<sub>12</sub> in radappertized chicken (Table 10). The electron-irradiated sample shows a much higher vitamin D content than does

either the gamma-irradiated or the frozen control sample. Since the value for electron-irradiated samples is much higher than for the frozen control or gamma-irradiated sample (Table 10), this work needs to be repeated in order to confirm these results.

TABLE 10  
DOSE RATE EFFECT ON FAT-SOLUBLE VITAMINS IN  
ENZYME-INACTIVATED RADAPPERTIZED CHICKEN<sup>1</sup>

Vitamin	Frozen Control	Gamma <sup>2</sup> (9.6 Gy/s) <sup>4</sup>	Electron <sup>3</sup> (10 <sup>6</sup> Gy/s) <sup>4</sup>
Vitamin A IU/kg <sup>5</sup>	2716.0	2270.0	2270.0
Vitamin D IU/kg	375.1	354.0	466.1
Vitamin K mg/kg	1.3	0.8	0.8
Vitamin B <sub>12</sub> µg/kg	8.3	13.7	8.8

1. Data from Thayer (1990).
2. <sup>60</sup>Co, irradiation dose 46-68 kGy at -25 ± 15°C.
3. 10-MeV electron accelerator dose, 45-68 kGy at -25 ± 15°C.
4. Thayer, personal communications.
5. IU/kg or µg and mg/kg of dry weight of chicken.

Lu et al. (1989) have observed lower or no loss of carotenoids in sweet potatoes at higher dose rates than at low dose rates (Table 6). However, the authors suggest that the longer irradiation times at 24°C played a role in the greater loss of carotenoids at the lower dose rate.

#### 4.2 MACRONUTRIENTS

Amino acids, proteins, carbohydrates and lipids are the macronutrients in foods. Many studies have focussed on the radiolysis of these components of foods and relevant model systems. The basic aspects of radiolysis that lead to chemical effects and the factors that influence these effects (irradiation temperature, oxygen effect, stability of free radicals) have been described (Singh 1987, 1988 and references therein). However, work on DRE has remained rather neglected.

##### 4.2.1 Amino Acids and Proteins

The radiation chemistry of amino acids and proteins remains an active field of research, owing to its relevance in radiobiology and food

irradiation (Biaglow et al. 1988, Davies 1988, Delincee 1983, Griffiths et al. 1988, Simic 1983, Singh and Singh 1982, Taub 1983). The range of possible chemical and physical changes from the irradiation of proteins in foods is similar to that from other treatments. Potential reactions include deamination, decarboxylation, reduction of disulfide linkages, oxidation of sulfhydryl groups, breakage of peptide bonds and changes in valency states of co-ordinated metal ions in enzymes (Delincee 1983, Taub 1983, Taub et al. 1979a). The products of protein irradiation include carbonyl compounds, ammonia, free amino acids, hydrogen peroxide and organic peroxides. Some free amino acid-protein bonding, protein-protein aggregation and cross-linking, and protein-lipid cross-linking can also occur, particularly at high doses. When proteins are irradiated, cross-linking and scission can proceed simultaneously (Bailey et al. 1964). Oxygen and the presence of radical scavengers inhibit cross-linking, as reported for collagen (Bailey 1967), whereas increasing protein concentrations favour cross-linking, as in the case of myoglobin (Lycometros and Brown 1973). The overall decomposition of proteins at low doses ( $\leq 10$  kGy at 1 to 4°C) and even at radappertization doses, is minimal.

#### 4.2.1.1 Amino Acids

While many amino acids in solution are susceptible to decomposition on irradiation at high doses (Diehl and Scherz 1975, Liebster and Kopoldova 1964), their sensitivities in meats are much lower (Partmann and Keskin 1979). Therefore, while a DRE may be expected in dilute solutions, it should become negligible in foods, as in the case of the micronutrients discussed in Section 4.1. This is supported by the available experimental data. Bound amino acids in proteins are known to be more stable against irradiation than free amino acids (Diehl and Scherz 1975, Maslennikova 1969, Rhodes 1966). From an analysis of the amino acids in beef, no significant differences were found between those irradiated in the frozen state ( $-30 \pm 10^\circ\text{C}$ ) to a dose of 47 to 72 kGy (by gamma or electron irradiation), the unirradiated controls and the thermally treated samples (Taub et al. 1979a). Table 11 gives the amino acid content of electron- and gamma-irradiated raw beef (6 kGy), as cited by Josephson et al. (1978 from the data of Frumkin et al. (1972)). These authors found no significant DRE on amino acid composition.

TABLE 11  
DOSE RATE EFFECT ON THE AMINO ACID CONTENT  
(g/100 g DRY WEIGHT OF PROTEIN) OF RAW BEEF<sup>1</sup>

Amino Acid	<sup>60</sup> Co Control Irradiation		Electron Irradiation			
			2 MeV		4 MeV	
	Dose Rate (Gy/s)					
	0	5.3	2 x 10 <sup>2</sup>	2 x 10 <sup>3</sup>	2 x 10 <sup>2</sup>	2 x 10 <sup>3</sup>
Cystine	0.72	0.86	0.71	0.87	0.65	0.62
Lysine and histidine	15.42	14.95	13.46	15.07	14.29	13.79
Arginine	7.95	7.23	7.72	8.09	7.32	7.65
Aspartic acid	7.04	7.15	6.85	6.65	6.41	6.78
Serine	2.82	2.79	2.97	2.60	3.04	2.96
Glycine	3.37	3.42	3.39	3.61	3.91	3.75
Glutamic acid	11.82	11.50	11.75	11.11	12.04	11.72
Threonine	4.64	4.67	4.23	4.52	4.52	4.54
Alanine	4.64	4.82	5.10	4.95	5.12	5.19
Tyrosine	2.84	3.03	2.74	2.89	3.02	2.77
Methionine	2.48	2.52	2.38	2.46	1.91	2.30
Valine	5.35	5.15	5.21	5.08	5.71	5.63
Phenylalanine	4.10	4.15	4.57	4.90	4.69	4.96
Leucine and isoleucine	9.19	9.32	10.04	9.74	9.96	9.93

1. Data cited by Josephson et al. (1978). Irradiation to a total dose of 6 kGy. Irradiation temperature not given but assumed to be ambient.

The electron and gamma irradiation of enzyme-inactivated beef at very low temperatures (-40°C) causes no significant DRE in terms of the loss of cystine, methionine or tryptophan, considered the most radiation-sensitive amino acids (Table 12, Josephson et al. 1978). An earlier study (Johnson and Moser 1967) compared the DRE on ground beef of gamma irradiation (<sup>60</sup>Co, 28 Gy/s) and electron-beam irradiation from an accelerator (11 and 24 MeV at 20 and 200 μA current levels), with dose rates of about 10<sup>8</sup> and 10<sup>9</sup> Gy/s respectively (also see Diehl 1982). The authors reached the following conclusions:

- (1) the destruction of amino acids in proteins by irradiation was limited to tryptophan and cystine, and

TABLE 12

DOSE RATE EFFECTS ON THE AMINO ACID CONTENT  
(WEIGHT PERCENT OF ENZYME-INACTIVATED BEEF<sup>1</sup>)

Amino Acid	T r e a t m e n t		
	Frozen Control	<sup>60</sup> Co (47-71 kGy)	10 MeV (47-71 kGy)
Cystine	0.28	0.26	0.28
Methionine	0.53	0.57	0.59
Tryptophan	0.25	0.25	0.26

1. Data from Josephson et al. (1978). Vacuum-packaged beef irradiated at -40°C.

(2) damage to amino acids was slightly less from gamma irradiation than from 24-MeV electron irradiation.

However, the latter conclusion is not supported by their data on tryptophan, histidine and cystine/cysteine. The data given in Table 13 generally indicate the following:

- (1) histidine and tryptophan losses are similar for gamma and electron (24-MeV) irradiation;
- (2) the differences in the case of cystine/cysteine are minor; and
- (3) there are wide and unexplained differences in amino acid losses from 11- and 24-MeV electron irradiation, even though, for the same current, the dose rate in the two cases would be expected to be similar.

The authors also report differences when the electron dose rate is increased by a factor of 10 for 11-MeV electrons which are not paralleled for 24-MeV electrons in the case of tryptophan (Table 13).

TABLE 13

CONCENTRATION (g/100 g PROTEIN) OF AMINO ACIDS IN GROUND BEEF  
AT AMBIENT TEMPERATURES, AT DIFFERENT DOSE RATES<sup>1</sup>

Radiation	11-MeV Electrons		24-MeV Electrons		<sup>60</sup> Co
	20 $\mu$ A	200 $\mu$ A	20 $\mu$ A	200 $\mu$ A	
Dose (kGy)	g/100 g protein				
<u>Tryptophan</u>					
0	1.703(100)	1.703(100) <sup>2</sup>	1.703(100)	1.703(100)	1.703(100)
20	1.665(98)	1.605(94)	1.498(88)	1.510(89)	1.477(87)
45	1.615(95)	1.575(93)	1.515(89)	1.485(87)	1.475(87)
100	1.595(94)	1.488(87)	1.505(88)	1.480(87)	1.475(87)
<u>Histidine</u>					
0	3.43	3.43	3.43	3.43	3.43
20	3.43	3.44	3.33	3.20	3.43
45	3.45	3.32	3.32	--	3.41
100	3.43	3.30	3.33	3.03	3.46
<u>Cystine/Cysteine</u>					
0	1.27(100)	1.27(100)	1.27(100)	1.27(100)	1.27(100)
20	1.11(87)	1.04(81)	0.92(72)	0.82(65)	0.89(70)
45	1.08(85)	0.96(76)	0.88(69)	0.74(58)	0.84(60)
100	1.08(85)	0.95(75)	0.83(65)	0.74(58)	0.84(66)

1. Data from Johnson and Moser (1967). Dose rate for gamma irradiation 28 Gy/s; for electron irradiation assumed to be 10<sup>8</sup> and 10<sup>9</sup> Gy/s respectively, from information given (20 and 200  $\mu$ A).
2. Numbers in brackets show percentage retention.

More recent data (Thayer 1990) on the amino acid content of gamma- and electron-radappertized chicken show no significant DRE (Table 14).

In general, therefore, considering all of the available data, it is concluded that there is no DRE on amino acids in foods.

TABLE 14  
CONTENT OF AMINO ACID (g/100 g PROTEIN) IN  
ENZYME-INACTIVATED CHICKEN TREATED WITH ELECTRONS AND GAMMAS<sup>1</sup>

Amino Acid	Frozen Control	Electron <sup>2</sup> (10 <sup>6</sup> Gy/s) <sup>4</sup>	Gamma <sup>3</sup> (9.6 Gy/s) <sup>4</sup>
Alanine	5.76	5.85	5.84
Arginine	6.24	6.38	6.37
Aspartic acid	8.94	8.84	8.98
Cysteine	0.91	0.93	0.96
Glutamic acid	14.33	14.17	14.19
Glycine	5.83	5.87	5.96
Histidine	4.05	4.36	4.21
Hydroxyproline	0.28	0.28	0.27
Isoleucine	4.51	4.67	4.70
Leucine	7.53	7.64	7.69
Lysine	8.34	8.49	8.55
Methionine	2.52	2.57	2.48
Phenylalanine	3.78	3.79	3.74
Proline	4.02	4.34	4.45
Serine	3.72	3.60	3.73
Threonine	4.11	3.94	4.14
Tryptophan	1.16	1.20	1.25
Tyrosine	3.38	3.22	3.34
Valine	4.79	4.93	5.02

1. Data from Thayer (1990).
2. 10-MeV electron-irradiated chicken, 45-68 kGy at -25 ± 15°C.
3. <sup>60</sup>Co, gamma-irradiated chicken, 46-68 kGy at -25 ± 15°C.
4. Thayer, personal communication.

#### 4.2.1.2 Proteins

Klein and Altmann (1972) reported some decrease in the molecular weight of soluble protein fractions at high doses (20 to 50 kGy), but no change at low doses (up to 7.5 kGy), under controlled temperature (4°C) was detected in irradiated chicken meat. On the other hand, Zabielski et al. (1984) have suggested that myosin solubility from chicken breast muscle is reduced with increasing irradiation dose (to 10 kGy), resulting in reduced water-holding capacity. Other protein solubilities were only slightly altered at these doses. The temperature during irradiation in these experiments was very high (up to 32°C), which may have affected their results. In contrast, Taub (1981, 1983) showed that sterilization doses at low temperatures have only a minor effect on myosin. His findings suggest that the irradiation of muscle proteins in meat does not lead to significant alteration and, therefore, is not of nutritional or physiological concern (Taub et al. 1977). However, no data are available to compare the effects of gamma and electron irradiation on the structural aspects of proteins, e.g., water-holding capacity and solubility.

Proteolytic enzymes are only partially inactivated at doses required for radurization (radiation pasteurization). Their inactivation depends on irradiation temperature and dose (Shults et al. 1975). For example, pork irradiated at 21°C loses about 75% of its proteolytic activity at a dose of 20 kGy, whereas the same meat irradiated at -30°C loses only about 60% of its activity, even when exposed to 40 kGy. Thus, the proteolytic and lipolytic enzymes are not fully inactivated at doses optimum for food irradiation (Diehl 1982, Josephson 1983). In fact, irradiation at low doses may increase the activities of some enzymes (Diehl 1982, Singh and Singh 1982). For example, the increase observed in levels of certain vitamins (Table 7) from the irradiation of meats could be due to the activation of relevant enzymes. Glew (1969) reported on what appears to be a DRE on the denaturation of the protein  $\beta$ -lactoglobulin in solution, at dose rates from  $10^5$  to  $10^7$  Gy/s (Table 15). The results show that the higher the dose rate the lower the degree of denaturation at a given dose. This denaturation effect was enhanced by the presence of oxygen (Glew 1969, results not shown). Apparently, no data on DRE on the cross-linking of proteins in foods have been reported.

TABLE 15  
DOSE RATE EFFECT ON DENATURATION OF 1% SOLUTION  
OF  $\beta$ -LACTOGLOBULIN<sup>1</sup>

Dose (kGy)	Dose Rate <sup>2</sup> (Gy/s)		
	1.11 x 10 <sup>7</sup>	1.11 x 10 <sup>8</sup>	1.11 x 10 <sup>9</sup>
	% Protein Denatured <sup>3</sup>		
2.5	37	19	14
3.5	37	24	20
5.0	52	35	32
7.5	65	44	38
10.0	73	60	56
15.0	84	71	78

1. Data from Glew (1969).
2. 4-MeV linear accelerator.
3. Denaturation was measured as the proportion of protein insoluble in 20% sodium sulphate solution at 40°C, at pH 2.

#### 4.2.2 Carbohydrates

The carbohydrates found in foods exist in forms ranging from aqueous solutions of simple sugars, as in fruit juices, to solid complex polysaccharides, such as starch in potatoes. Despite these differences, their radiation chemistry is quite similar (Taub 1983). This similarity stems from the structural similarity of the sugars to each other and from the fact that the polysaccharides are composed of repeating units of a small number of sugars.

Fundamental changes that can occur in carbohydrates are similar to those that take place in proteins and include decomposition (degradation) and cross-linking. Hexoses are degraded by dehydrogenation and complex polysaccharides exhibit breaks in the glycosidic linkages. Though many of these radiolytic aspects have been investigated, very little work has been done on DRE on carbohydrates in foods. In dilute solutions, DRE is observed from the irradiation of glucose solution (Simic 1983), as

shown by the yields (G-values) of some of its products (Table 16). The G-values for these products are lower at the high dose rates delivered by electron irradiation. Somogyi et al. (1975) reported work on DRE on the carbohydrate content of two varieties of potatoes ( Bintje and Maritta). The potatoes were irradiated using 3-MeV electrons (dose rate not given) and  $^{60}\text{Co}$  (dose rate 1.7 Gy/s) for total doses of 0.08, 1 and 1.5 kGy. The results for the Bintje variety are shown in Figure 10. Any differences in the resulting glucose and sucrose levels from electron and gamma irradiation are minor. However, there appears to be a larger increase in the fructose content (Figure 10) in the case of electron irradiation than in the case of gamma irradiation, at the higher total doses (>1 kGy). Lu et al. (1987) saw somewhat greater sugar loss in onions subjected to gamma irradiation ( $^{60}\text{Co}$ ; dose rate 22.8 Gy/s) than in those subjected to electron irradiation (2-MeV Van de Graaff; dose rate not given); the authors suggest that this difference may lie in the shallow penetration of onions by the electron beam, as one might expect, and thus may not be a true DRE.

TABLE 16

RADIOLYSIS OF AQUEOUS SOLUTION OF D-GLUCOSE:  
DOSE RATE EFFECT<sup>1,2</sup>

Product	G-Value	
	Electron <sup>3</sup>	Gamma <sup>4</sup>
D-Gluconic acid	0.80	0.90
D-Arabinohexosulose	0.61	0.90
D-Ribohexos-3-ulose	0.40	0.57
D-Xylohexos-4-ulose	0.41	0.50
D-Xylohexos-5-ulose	0.20	0.60
D-Glucohexodialdose	0.90	1.55

1. Data from Simic (1983).
2. Radiolysis in  $\text{N}_2\text{O}/\text{O}_2$  (4:1) saturated aqueous solution at room temperature.
3. Van de Graaff, electron-irradiated  $5 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$  D-glucose solution at 2.5 Gy/pulse (4-Hz frequency, 1- $\mu\text{s}$  pulse).
4.  $^{60}\text{Co}$ , gamma-irradiated,  $5 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$  D-glucose solution at 0.18 Gy/s.

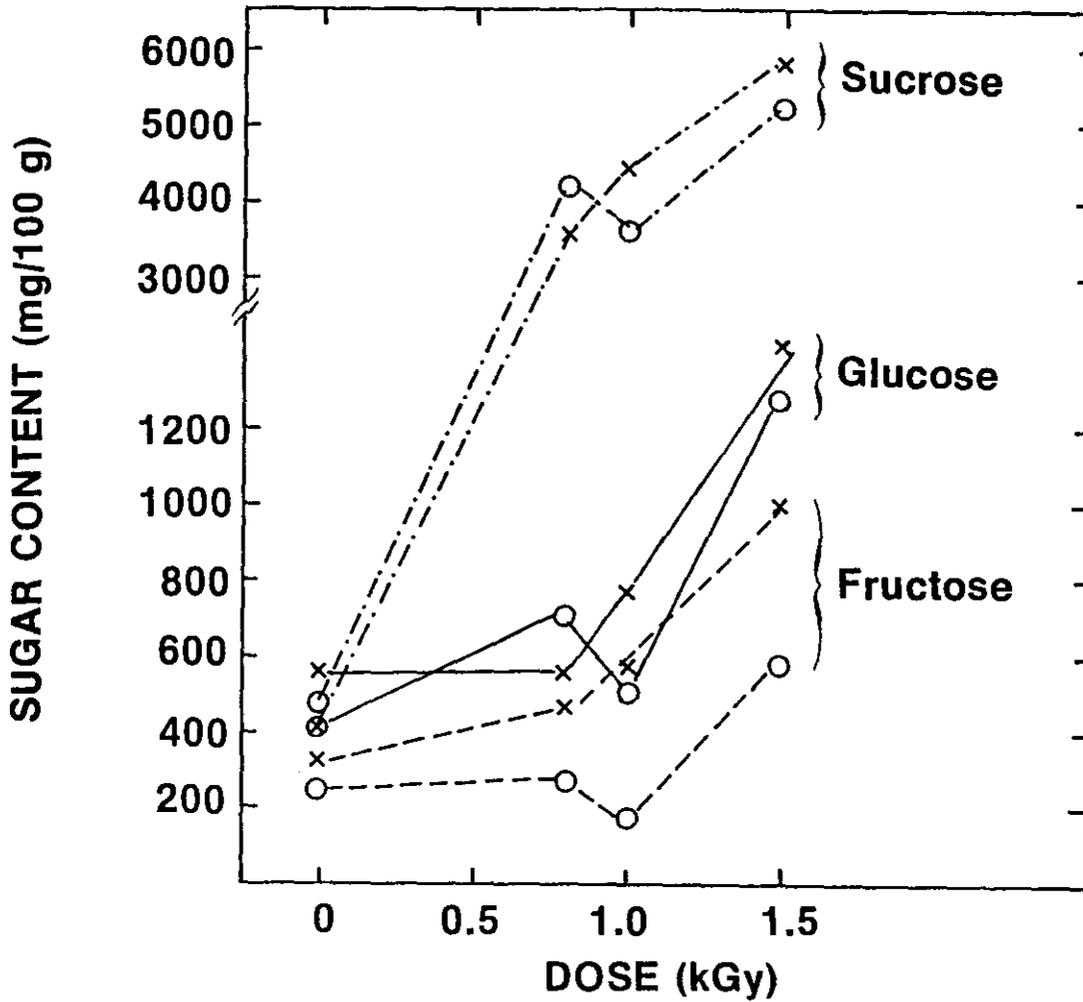


FIGURE 10: Effect of Gamma and Electron Irradiation on Sugar Content in Potatoes (Bintje). Data from Somogyi et al. (1975). X = electron irradiation (3-MeV, dose rate not given but assumed to be  $10^6$  Gy/s); o = gamma irradiation (dose rate 6.3 kGy/h).

#### 4.2.3 Lipids

Lipids are a heterogeneous group of organic compounds that make up a large proportion of the human diet. They are distributed widely in both plant and animal tissue and influence many qualities of foods including contributions of essential nutrients, energy, mouth-feel, flavor, and emulsifying and complexing characteristics. The physical and chemical makeup of lipids in foods, whether natural or added, can be greatly altered by processing, and these changes may be either beneficial or detrimental.

Lipids containing unsaturated fatty acids are readily auto-oxidized, and enzymatically oxidized, during normal chemical and metabolic activity. They are also oxidized during irradiation in the presence of oxygen. Irradiation in air produces volatile products by the process of lipid peroxidation. However, these effects can be minimized by irradiation at low temperatures (Brasch and Huber 1947, Merritt 1984, Wierbicki 1985, Singh 1987) and in the absence of oxygen (Kraybill 1982, Merritt et al. 1985, Singh 1987). Most of these oxidizing reactions proceed through free radicals (Delincee 1983; Nawar 1983; Taub 1983; Singh 1987, 1988). Some of the many products formed from such oxidations, such as peroxides, hydroperoxides and carbonyl compounds (ketones and aldehydes), can affect the flavor of meat, including the development of off-flavors (Merritt et al. 1978, Merritt and Taub 1983, Lillard 1978, Pearson et al. 1983, Pryor et al. 1976, Francis and Wood 1982, Singh 1988). However, it is generally reported that at low doses and controlled temperature conditions (0-5°C), irradiation has no significant effect on the total fat content of foods (of chicken, for example; Kahan and Howker 1978). Only minor differences have been reported in fatty acid profiles (Food Chemical News, 1987) by irradiation at 1 to 10 kGy.

As discussed in Section 2.3 above, lipid peroxidation levels in foods may be slightly lower after electron irradiation than after gamma irradiation. This view is reflected in a review article by Kraybill

(1982). Unfortunately, as there seem to be no data directly comparing lipid peroxidation levels after electron and gamma irradiation, the expectation of lower peroxidation after electron irradiation remains to be tested. While two studies do give the peroxide values for enzyme-inactivated radappertized chicken rolls (Wierbicki 1985, Table 17) and beef (Raica et al. 1972), these data are not relevant to lipid peroxidation in air, since the samples were vacuum-packaged in the absence of oxygen.

Wierbicki (1985) also published data on free fatty acids produced in low-temperature ( $-25 \pm 15^\circ\text{C}$ ) electron- and gamma-radappertized chicken rolls (Table 17) during storage at ambient temperatures. The results indicated no DRE after 3 or 81 months of storage. Similarly, no significant DRE on total free fatty acids or individual fatty acids was seen by Thayer (1990) in the case of radappertized chicken.

TABLE 17  
EFFECT OF DOSE RATE AND STORAGE ON PEROXIDE VALUE  
AND FREE FATTY ACID CONTENT OF CHICKEN ROLLS<sup>1</sup>

Fat Oxidation Index <sup>4</sup>	Frozen Control		Gamma <sup>2</sup>		Electron <sup>3</sup>	
	Storage Time (months)					
	3	81	3	81	3	81
Peroxide value	38.1	1.6	11.3	0.6	14.1	0.9
Free fatty acid	0.7	0.9	0.9	4.6	0.9	5.0

1. Data from Wierbicki, 1985. Irradiation dose 46-68 kGy at  $-25 \pm 15^\circ\text{C}$ .
2.  $^{60}\text{Co}$ , dose rate  $\sim 5 \times 10^2$  Gy/s.
3. 10-MeV linear electron accelerator, dose rate not given but, based on Shults and Wierbicki (1980), assumed to be  $\sim 10^6$  Gy/s.
4. Peroxide value as milliequivalent  $\text{O}_2/\text{kg}$  fat, free fatty acid as % oleic acid in extracted fat.

#### 4.3 VOLATILE COMPOUNDS

As discussed above (Section 4.2.3) enzymatic reactions, auto-oxidation and irradiation produce small-molecular-weight volatile components, such as aldehydes and ketones, from fats that impart particular flavors to foods. Similarly, some products obtained from proteins, such as sulfur-containing compounds, impart characteristic flavors to meats. In addition, a number of other classes of organic compounds, including furans and chlorinated compounds, are related to meat flavors and off-flavors (Ramaswamy and Richards 1982, Merritt et al. 1978, Merritt 1984). In irradiated meats, the undesirable components (off-flavors) are produced as a function of radiation dose and temperature (Merritt et al. 1975); their levels are reduced by irradiation at subfreezing temperatures. The volatile compounds from chicken, pork, beef and other meats are qualitatively similar (Merritt 1972, Merritt et al. 1975).

The DRE on the volatiles formed from many of these meats has been compared by Merritt (1984). The effect of irradiation at a dose of 45 kGy at  $-30^{\circ}\text{C}$ , is shown by the data on the low-molecular-weight volatiles in Table 18. Although the Table indicates some differences in the absolute numbers for various volatiles, both between gamma and electron irradiation and between different production lots, the authors suggest in one publication (Merritt et al. 1978) that the amounts of volatile products obtained are independent of the type of radiation used, based on the statistical evaluation of their original data. However, it is not clear whether the statistical analyses and the conclusion that no DRE is present (Merritt et al. 1978) apply to all other data reported by this group (Merritt 1984).

Data for the solvent-extracted high-molecular-weight volatiles from chicken are compared in Table 19 (Merritt 1984). Clearly, different absolute amounts of some volatiles, such as octadecenal, are produced by gamma and electron irradiation. In both the low-molecular-weight (Table 18) and the high-molecular-weight (Table 19) volatile compounds, the electron-irradiated (high dose rate) chicken samples appear to give higher yields than the gamma-irradiated samples. Also, the values of many of the products differ between the two production lots (Table 18). However, it is not clear whether these differences are important.

**TABLE 18**  
**VOLATILE RADIOLYSIS PRODUCTS ISOLATED FROM CHICKEN MEAT**  
**BY DIFFERENT TREATMENTS<sup>a</sup>**

	Frozen Control		Gamma Irrad.		Electron Irrad.	
	No. 1 <sup>b</sup>	No. 2 <sup>b</sup>	No. 1 <sup>b</sup>	No. 2 <sup>b</sup>	No. 1 <sup>b</sup>	No. 2 <sup>b</sup>
1 Ethane			110	134	161	196
2 Propane			116	129	167	205
3 N-Butane			109	137	172	195
4 Isobutane			17	22	24	30
5 N-Pentane	2	3	107	138	157	191
6 Isopentane			11	16	14	19
7 N-Hexane	9	5	173	219	248	301
8 2-Methylpentane			-	+	2	1
9 3-Methylpentane			-	-	-	+
10 N-Heptane	12	8	271	235	392	477
11 N-Octane			336	331	489	598
12 Methylheptane	5	4	4	3	+	-
13 N-Nonane			101	131	153	187
14 N-Decane			135	149	208	232
15 Undecane			182	191	280	303
16 Dodecane			242	253	373	398
17 Tridecane			89	93	137	151
18 Tetradecane			12	13	18	20
19 Ethene			13	21	21	26
20 Butene			16	23	22	27
21 Pentene			93	186	135	164
22 Hexene	+	-	67	95	98	114
23 Heptene	+	+	115	107	169	207
24 Octene			241	156	347	427
25 Nonene			51	55	79	86
26 Decene			115	123	177	195
27 Undecene			92	97	142	158
28 Dodecene			164	171	253	278
29 Tridecene			56	59	86	95
30 Tetradecene			85	92	109	123
31 Benzene			12	14	18	20
32 Toluene	1	+	28	31	43	48
33 Xylene			1	2	2	2
34 Methyl alcohol			31	35	48	52
35 Ethyl alcohol			50	55	77	84
36 Acetone	1	1	41	43	63	69
37 Butanone	+	1	16	17	25	27
38 Acetaldehyde	-	-	77	81	119	131
39 Carbonyl sulfide			-	+	-	+
40 Hydrogen sulfide			+	+	+	+
41 Methyl mercaptan			+	+	+	+
42 Ethyl mercaptan			6	7	3	6
43 Dimethyl sulfide	+	+	3	4	4	3
44 Dimethyl disulfide	-	-	16	14	15	19
45 Methylthiophene	0	0				
46 Ethane nitrile			+	+	+	0
47 Dimethylfuran	+	+				
48 Chloroform	12	8	13	8	8	13
49 Decyne			26	25	40	44
50 Undecyne			13	15	20	22
51 Dodecyne			6	7	9	10
52 Tridecadiene			+	-	+	-
53 Tetradecadiene			17	17	26	28

<sup>a</sup> Based on data of Merritt (1984), given in units of microgram of product per kilogram of chicken meat. Samples were irradiated at -30°C for 45-kGy total dose.  
<sup>b</sup> Samples from two different production lots (No. 1 and No. 2) were processed simultaneously.

TABLE 19

MAJOR ORGANIC EXTRACTABLE HIGH-MOLECULAR-WEIGHT  
RADIOLYTIC PRODUCTS FORMED IN CHICKEN MEAT  
BY GAMMA AND ELECTRON IRRADIATION<sup>1</sup>

Product	Cobalt-60 <sup>b</sup>	Linear Accelerator <sup>2</sup>
	mg/g	mg/g
Pendadecane	0.003	0.04
Heptadecene	0.035	0.045
Hexadecanal	0.038	0.055
Octadecenal	0.015	0.05
Ethyl palmitate	0.01	0.01
Ethyl oleate	0.006	0.006
16/16 propanediol diesters	0.006	0.0065
16/18:1 propanediol diesters	0.015	0.018

1. Based on data from Merritt (1984).

2. Dose 45 kGy at -30°C.

It should be pointed out here that, in general, somewhat higher amounts of volatile compounds appear to be generated by electron irradiation than by gamma irradiation. However, it is not certain whether the differences are significant and outside the overall experimental error.

#### 4.4 SPROUTING

Even though some data in the literature are contradictory (Kahan and Temkin-Gorodeiski 1968, Thomas 1984) there is sufficient evidence from a number of studies (Kume et al. 1976, 1977, Furuta et al. 1979, Mathur 1963) that suggests a DRE on sprout inhibition in potatoes and onions. A comparison of the DRE on sprouting is shown in Table 20.

Although a DRE on sprouting is seen in many varieties of potatoes, each variety has a different optimal dose requirement, which must be determined. For example, Mathur (1963) reported optimal total doses of 60 and 90 Gy for the potato varieties Gola and Up-to-Date respectively. Data for DRE on the two varieties are shown in Table 21.

TABLE 20

DOSE RATE, TOTAL DOSE AND TIME OF IRRADIATION USED FOR  
COMPARATIVE SPROUT INHIBITION IN POTATOES AND ONIONS

Number of Product Varieties	Total Dose (Gy)	Dose Rate (Gy/s)		Conclusion <sup>1</sup>	Reference
		High	Low		
<u>Potatoes</u>					
3	- <sup>2</sup>	100	0.016	HDR-B	Jaarma (1969)
2	60 90	30(2) <sup>3</sup> 30(3)	2.5(24) 2.5(36)	HDR-B HDR-B	Mathur (1963)
1	50	6.3(7.9)	0.4(125)	HDR-B	Kruschev et al. (1964)
1	70	12(5.8)	1.0(70)	HDR-B	Metlitsky et al. (1968)
1	-	0.45	0.04	HDR-B	Scheid and Heilinger (1968)
1	105	83	0.083	HDR-B <sup>4</sup>	Furuta et al. (1979)
1	100-140	12.6(7.9-11)	3.16(79-110)	NAD	Kahan and Temkin-Gorodeiski (1968)
1	50-70	16.6	0.83	NAD	Kume et al. (1976)
<u>Onions</u>					
1	20	83	0.083	HDR-B <sup>5</sup>	Furuta et al. (1979)
1	100	2 MeV <sup>6</sup>	22.8	NAD	Lu et al. (1987)
1	30 and 50	16.7	0.83	HDR-B	Kume et al. (1977)

1. HDR-B, high dose rate is better; NAD, no apparent dose rate effect.
2. Not available.
3. Numbers in brackets indicate calculated times (min) of irradiation.
4. Optimum dose rate 0.83 Gy/m.
5. Optimum dose rate 0.166 Gy/m.
6. Dose rate not given.

TABLE 21

DOSE RATE EFFECT ON PERCENTAGE OF TUBER SPROUTING  
IN TWO VARIETIES OF POTATOES<sup>1</sup>

Potato Variety	Total Dose (Gy)	Dose Rate (Gy/m)		
		0	2.5	30
		Percent Sprouting		
Gola	60	100	15	0
Up-to-Date	90	100	20	0

1. Data taken from Mathur (1963).

Furuta et al. (1979) and Kume et al. (1977) observed a DRE on onion sprouting in which a higher dose rate had a greater inhibitory effect than a low dose rate, although Lu et al. (1987) observed no difference at the dose relevant for sprout inhibition (100 Gy). The DRE on the inhibition of onion sprouting is shown in Figure 11. Furuta et al. (1979) observed that the dose required for complete sprout inhibition on onion bulbs was about 20 Gy at a dose rate of 10 Gy/h. Below 10 Gy/h the dose required increased rapidly, while above 10 Gy/h it decreased slowly with increasing dose rate (Figure 11). It appears therefore that this is a genuine DRE, since the increase in dose rate reduced the total dose required for sprouting.

5. SENSORY CHARACTERISTICS

The measurement of sensory or organoleptic characteristics and the determination of consumer product acceptance represent very important and necessary steps in food processing. The former is usually conducted by trained taste panels and the latter by randomly chosen consumer groups. The two are, of course, complementary.

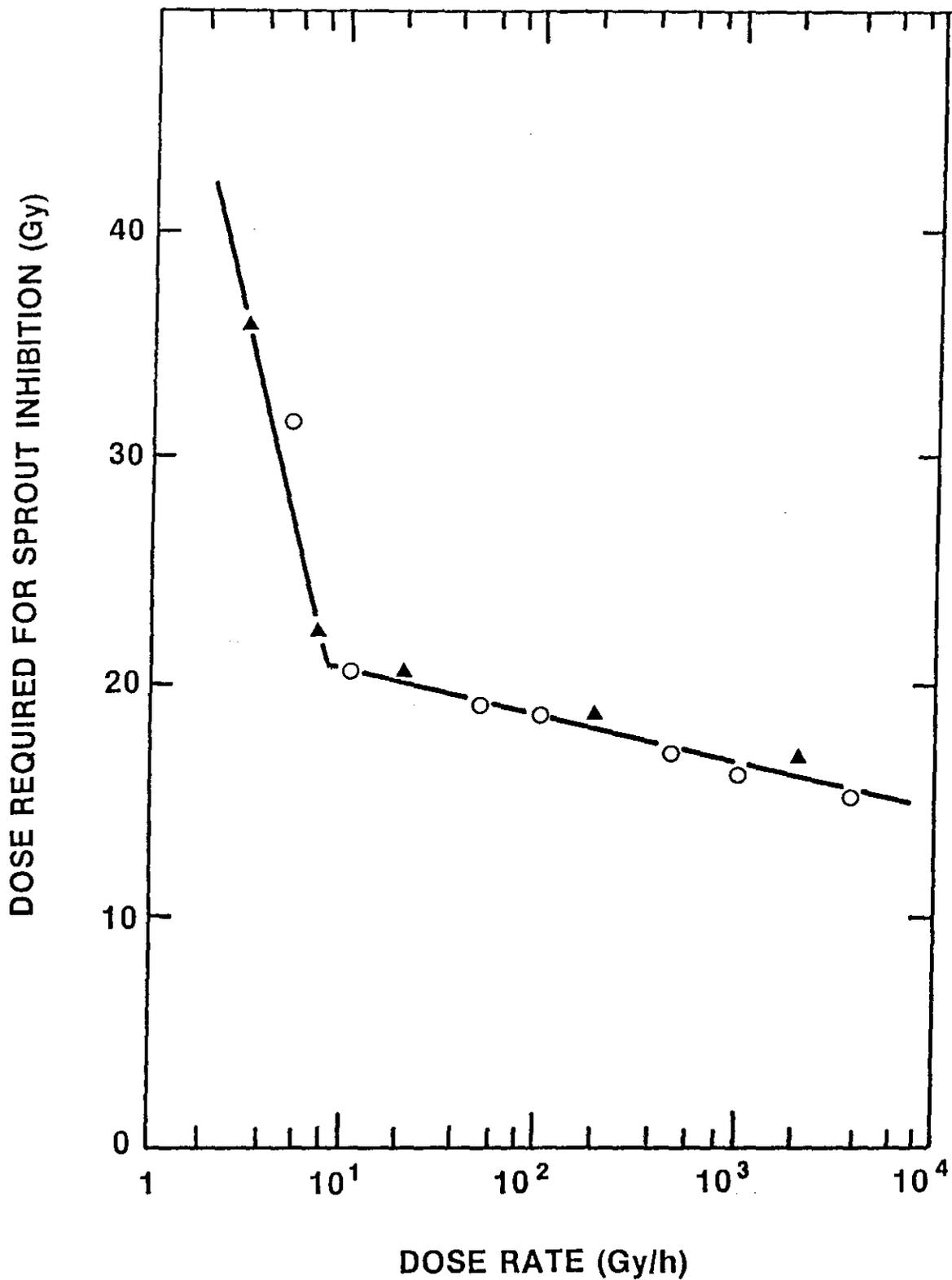


FIGURE 11: Dose Required for Inhibition of Sprouting of Onion Bulbs After 8 Months of Storage as a Function of Dose Rate. Values obtained during 1976-77, o - o and 1977-78, ▲ - ▲. Data from Furuta et al. (1979).

Some data are available on DRE on the sensory characteristics of irradiated food. Josephson et al. (1973) have reported consumer acceptance test results for gamma- and electron-irradiated roast beef. As the data in Table 22 show, there is no significant difference in the average preference ratings for the two types of irradiation.

Shults and Wierbicki (1980) described their results from the sensory evaluation of gamma- and electron-radappertized lamb rolls (dose 47 kGy). The data in Table 23 indicate no significant differences in terms of sensory characteristics between samples irradiated at two different dose rates (gamma,  $\sim 5 \times 10^2$  Gy/s and electron,  $\sim 10^6$  Gy/s). Though the authors do not make a distinction, the scores for the frozen control appear to be somewhat better than for either of the irradiated samples. The authors found no change in the results shown in Table 23, whether the samples were analyzed after zero, one or six months of storage.

TABLE 22  
CONSUMER ACCEPTANCE OF ROAST BEEF  
IRRADIATED WITH GAMMA OR ELECTRONS<sup>1</sup>

Experiment No.	No. of Raters	Average Preference Rating <sup>2</sup>		
		<sup>60</sup> Co <sup>3</sup>	Electron <sup>3</sup>	Control
1	32	5.5	5.4	5.5
2	32	6.2	5.6	6.1
3	32	5.4	5.8	6.0
4	32	6.6	5.9	6.2
5	32	5.6	6.3	6.0
6	30	5.0	5.6	4.8
7	30	5.8	6.3	5.4

1. Data from Josephson et al. (1973).
2. Nine-point hedonic scale: 9 = like extremely; 5 = neither like nor dislike; 1 = dislike extremely.
3. Irradiation dose 47 to 71 kGy at  $-30 \pm 10^\circ\text{C}$ .

TABLE 23

SENSORY CHARACTERISTICS OF GAMMA- AND ELECTRON-IRRADIATED LAMB ROLLS<sup>1</sup>

Sample	Discoloration	Off-Odor	Irradiation Flavor	Mushiness
Gamma	1.9 ± 0.81	1.9 ± 0.99	2.0 ± 1.20	2.4 ± 1.29
Electron	1.7 ± 0.70	2.1 ± 0.99	2.0 ± 1.50	2.4 ± 1.50
Frozen control	1.0 ± 0.00	1.0 ± 0.00	1.0 ± 0.00	1.6 ± 0.73

1. Data from Shults and Wierbicki (1980). Irradiation dose 47 kGy at  $-30 \pm 10^{\circ}\text{C}$ ; seven-member trained panels, probably nine-point scale. Characteristics ranged from 1 = none, 2 = trace, 3 = slight to 9 = extreme. Gamma dose rate,  $\sim 5 \times 10^2$  Gy/s; electron dose rate (10-MeV LINAC),  $\sim 10^6$  Gy/s.

Wierbicki (1985) has published the results of expert panel evaluation (Table 24) and consumer acceptance (Table 25) of gamma- and electron-radappertized chicken meat. In general, no significant

TABLE 24

EXPERT PANEL EVALUATION OF DOSE RATE EFFECT ON THE SENSORY CHARACTERISTICS OF ENZYME-INACTIVATED RADAPPERTIZED CHICKEN MEAT<sup>1</sup>

Treatment	Overall Score <sup>2</sup>			
	Colour	Odor	Flavor	Texture
Gamma <sup>3</sup>	6.28 <sup>b</sup> ± 0.73 <sup>6</sup>	6.04 <sup>a</sup> ± 0.53 <sup>6</sup>	5.43 <sup>a</sup> ± 0.38 <sup>6</sup>	5.40 <sup>b</sup> ± 0.58 <sup>6</sup>
Electron <sup>4</sup>	6.30 <sup>b</sup> ± 0.73	5.98 <sup>a</sup> ± 0.58	5.40 <sup>a, b</sup> ± 0.56	5.35 <sup>b</sup> ± 0.54
FC <sup>5</sup>	6.45 <sup>b</sup> ± 0.44	6.68 <sup>b</sup> ± 0.48	6.40 <sup>b</sup> ± 0.47	6.11 <sup>c</sup> ± 0.42

1. Data from Wierbicki (1985).
2. Expert panel, n = 10; Average data for 4 storage times x 2 preparations for serving (n = 80). Details of cooking conditions not given.
3. <sup>60</sup>Co, dose rate  $\sim 5 \times 10^2$  Gy/s.
4. 10-MeV LINAC  $\sim 10^6$  Gy/s (Shults and Wierbicki 1980).
5. Frozen control.
6. Mean values with different superscripts in the same column (a, b, c) are significantly different (P < 0.05).

TABLE 25

CONSUMER PREFERENCE RATINGS OF GAMMA- AND  
ELECTRON-IRRADIATED CHICKEN MEAT<sup>1</sup>

Treatment <sup>2</sup>	Rating
<u>Served Cold</u>	
Gamma-irradiated	5.00 <sup>a</sup> ± 1.64 <sup>3</sup>
Electron-irradiated	4.62 <sup>a</sup> ± 1.77
Frozen control	6.37 <sup>b</sup> ± 1.60
<u>Served Reheated</u>	
Gamma-irradiated	5.78 <sup>a</sup> ± 1.64
Electron-irradiated	5.91 <sup>a</sup> ± 1.91
Frozen control	6.88 <sup>b</sup> ± 1.45

1. Data from Wierbicki (1985). Nine-point hedonic scale: 9 = like extremely; 5 = neither like nor dislike; 1 = dislike extremely.
2. Gamma irradiation dose 56 kGy (dose rate ~ 5 x 10<sup>2</sup> Gy/s) and electron irradiation dose 59 kGy (dose rate ~ 10<sup>6</sup> Gy/s; Shults and Wierbicki 1980); irradiation at -30°C; the unirradiated controls from the same batch were kept frozen at -29°C until required.
3. Mean values with different superscripts (a, b) in the same column are significantly different (P < 0.05).

differences were found between gamma- and electron-irradiated chicken meat in either set of data (Table 24 and 25). The consumer preference ratings for (electron- or gamma-) irradiated chicken meat were significantly lower than those for the controls, particularly in the case of chicken meat served cold (Table 25). Wierbicki (1985) reported better consumer preference ratings in a subsequent run involving a lower radappertization dose (45 to 55 kGy) and a better temperature control (-30 ± 10°C).

Lu et al. (1987) have reported a comparison of onions irradiated to doses of 5 kGy with either an electron or a gamma source (Table 26). Even though the authors report some differences at the 5% level, their overall evaluation is that there are no major differences.

**TABLE 26**  
**SENSORY EVALUATION OF GAMMA- AND ELECTRON-IRRADIATED**  
**WALLA WALLA ONIONS<sup>1</sup>**

Irradiation Treatment	Fresh			Cooked <sup>2</sup>			
	Dose (kGy)	Firmness	Flavor	Taste	Firmness	Flavor	Taste
None	0	7.0 <sup>a</sup>	6.7 <sup>b</sup>	6.4 <sup>a</sup>	6.4 <sup>a</sup>	4.8 <sup>b</sup>	4.9 <sup>c</sup>
Electron (2 MeV)	0.1	6.1 <sup>a</sup>	7.3 <sup>a</sup>	6.8 <sup>a</sup>	7.3 <sup>a</sup>	7.3 <sup>a</sup>	7.0 <sup>a</sup>
	1.0	6.6 <sup>a</sup>	6.7 <sup>ab</sup>	6.6 <sup>a</sup>	5.9 <sup>3</sup>	5.5 <sup>ab</sup>	5.4 <sup>bc</sup>
	2.0	6.8 <sup>a</sup>	5.6 <sup>b</sup>	6.4 <sup>a</sup>	7.0 <sup>a</sup>	6.5 <sup>ab</sup>	7.0 <sup>a</sup>
	3.0	6.7 <sup>a</sup>	6.7 <sup>ab</sup>	6.7 <sup>a</sup>	8.6 <sup>a</sup>	6.6 <sup>ab</sup>	5.7 <sup>b</sup>
	5.0	6.7 <sup>a</sup>	5.6 <sup>b</sup>	5.9 <sup>a</sup>	7.0 <sup>a</sup>	6.2 <sup>ab</sup>	6.7 <sup>ab</sup>
None	0	6.6 <sup>abc</sup>	6.4 <sup>a</sup>	6.6 <sup>ab</sup>	7.1 <sup>a</sup>	6.5 <sup>a</sup>	7.0 <sup>a</sup>
Gamma (22.8 Gy/s)	0.1	6.2 <sup>abc</sup>	6.0 <sup>a</sup>	6.0 <sup>b</sup>	6.8 <sup>ab</sup>	6.3 <sup>a</sup>	6.5 <sup>a</sup>
	0.3	7.4 <sup>a</sup>	7.3 <sup>a</sup>	7.6 <sup>a</sup>	8.0 <sup>a</sup>	7.3 <sup>a</sup>	7.0 <sup>a</sup>
	1.0	7.0 <sup>ab</sup>	7.2 <sup>a</sup>	7.1 <sup>ab</sup>	6.4 <sup>ab</sup>	5.5 <sup>a</sup>	5.9 <sup>a</sup>
	2.0	6.8 <sup>abc</sup>	6.6 <sup>a</sup>	6.5 <sup>ab</sup>	6.7 <sup>ab</sup>	6.2 <sup>a</sup>	5.9 <sup>a</sup>
	3.0	5.6 <sup>c</sup>	6.5 <sup>a</sup>	6.0 <sup>b</sup>	5.5 <sup>b</sup>	5.7 <sup>a</sup>	5.5 <sup>a</sup>

1. Data from Lu et al. (1987). A nine-point hedonic scale was used for sensory evaluation: 9 = like extremely; 1 = dislike extremely. Mean values with the same superscripts (a, b, c) in the same columns are not different (P < 0.05).
2. Chopped onions were cooked for 2 min at 250°C.

## 6. CONCLUSIONS

Basic mechanistic considerations suggest that, although the loss of key micro- and macronutrients in dilute solutions are expected to be lower from electron irradiation (high dose rate) than from gamma irradiation (low dose rate), the difference, if any, should be negligible for irradiated foods. Experimental data comparing gamma and electron irradiation of foods, though rather limited, do support this expectation. Available results give no indication of any DRE on amino acids, proteins, carbohydrates, fats, or most of the vitamins in irradiated foods. However, a DRE favoring electron irradiation over gamma irradiation has been reported in two processes:

- (1) Thiamin loss in pork and other meats is significantly lower from electron irradiation than from gamma irradiation, at low temperatures (-15 to -45°C). Spur diffusion is much slower at these temperatures than at 0°C, leading to significant spur overlap in the case of electron irradiation. In comparison, no spur overlap is likely in the case of gamma irradiation at low temperatures, even with slower spur diffusion. Hence the observed DRE on thiamin in the low-temperature irradiation of meats, favoring electron irradiation.
  
- (2) Sprouting in potatoes and onions is inhibited more effectively by electron irradiation than by gamma irradiation. However, the mechanistic reasons for this effect are unknown.

Mechanistic considerations suggest that electron irradiation may also be favoured over gamma irradiation for foods normally irradiated in air, since electron irradiation should result in lower peroxidation levels in the food. However, experimental data supporting such a conclusion are unavailable.

While computer modelling of irradiation of simple systems is being done, no data are available from which to predict a DRE in the case of irradiated foods on this basis.

Somewhat higher amounts of volatile compounds appear to be generated by electron irradiation than by gamma irradiation. However, it is not certain whether the differences are significant and outside the overall experimental error.

The sensory characteristics, as judged by expert panels and rated by consumer acceptance panels, show no significant differences between gamma- and electron-irradiated foods, thus supporting the overall conclusion that the two irradiation methods are equally effective.

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APPENDIX A

SPUR OVERLAP: AN ESTIMATE

The calculations below are aimed at establishing ballpark figures on the dose rates required to achieve spur overlap. For this purpose, two cases are considered: the initial spur and the semidiffused spur, with diameters of 4.6 and 460 nm respectively. These calculations are semi-quantitative and valid only for the assumptions made below.

A.1 4.6-nm SPUR IN LIQUID WATER

It is assumed that, if the spur volume exceeds 5% of the total volume during a 0.1-ns pulse, significant spur overlap will occur.

(a) Volume of a spur:

$$\begin{aligned} &= \frac{4}{3} \pi r^3 = \frac{4}{3} \times 3.14 \times (2.3 \times 10^{-7})^3 \text{ cm}^3 \\ &= 5.1 \times 10^{-20} \text{ cm}^3 \end{aligned}$$

(b) Number of spurs required to occupy 5% of the sample volume, i.e., 0.05 cm<sup>3</sup> in 1 cm<sup>3</sup> water:

$$= \frac{5 \times 10^{-2}}{5.1 \times 10^{-20}} = 1 \times 10^{18}$$

(c) The dose per spur is 62.5 eV (Schwartz 1969).

Therefore, the dose required to produce 1 x 10<sup>18</sup> spurs per cm<sup>3</sup>:

$$\begin{aligned} &= 62.5 \times 10^{18} \text{ eV} \\ &= \frac{62.5 \times 10^{18}}{6.24 \times 10^{13} \times 10^2} \text{ Gy} \\ &= 10^4 \text{ Gy} \end{aligned}$$

(d) Dose rate, Gy/s.

Since the dose required is 10<sup>4</sup> Gy per 0.1 ns (10<sup>-10</sup> s), the dose rate required:

$$\begin{aligned} &= \frac{10^4}{10^{-10}} \text{ Gy/s} \\ &= 10^{14} \text{ Gy/s} \end{aligned}$$

#### A.2 460-nm SPUR IN LIQUID WATER

It is assumed that the time required for the spur to diffuse from a diameter of 4.6 nm to 460 nm is about  $5 \times 10^{-8}$  s. Therefore, if the spur volume exceeds 5% of the total volume during a  $5 \times 10^{-8}$ -s pulse, significant spur overlap will occur.

(a) Volume of a spur:

$$\begin{aligned} &= \frac{4}{3} \pi r^3 = \frac{4}{3} \times 3.14 \times (2.3 \times 10^{-5})^3 \text{ cm}^3 \\ &= 51 \times 10^{-15} \text{ cm}^3 \end{aligned}$$

(b) Number of spurs required to occupy 5% of the sample volume, i.e., 0.05 cm<sup>3</sup> in 1 cm<sup>3</sup> water:

$$= \frac{5 \times 10^{-2}}{5.1 \times 10^{-14}} = 1 \times 10^{12}$$

(c) Dose required to produce  $1 \times 10^{12}$  spurs per cm<sup>3</sup>:

$$\begin{aligned} &= 10^{12} \times 62.5 \text{ eV} \\ &= \frac{62.5 \times 10^{12}}{6.24 \times 10^{13} \times 10^2} \text{ Gy} \\ &= 10^{-2} \text{ Gy} \end{aligned}$$

(d) Dose rate, Gy/s.

Since the dose required is  $10^{-2}$  Gy per  $5 \times 10^{-8}$  s, the dose rate required:

$$\begin{aligned} &= \frac{10^{-2}}{5 \times 10^{-8}} \text{ Gy/s} \\ &= 2 \times 10^5 \text{ Gy/s} \end{aligned}$$

Thus, in liquid water or aqueous solutions, different degrees of spur overlap may occur at doses greater than  $10^8$  Gy/s. In order to achieve spur overlap of initial, undiffused spurs, dose rates greater than  $10^{14}$  Gy/s are required.

In the case of frozen samples and solids, spur overlap may occur at much lower dose rates, owing to the much higher viscosities and, consequently, much lower spur diffusion rates of the systems.

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APPENDIX B

RADIOLYTIC REACTIONS OF WATER

TABLE B-1

SET OF CHEMICAL REACTIONS, WITH CORRESPONDING  
RATE CONSTANTS, DURING RADIOLYSIS OF WATER

<u>REACTION</u>	<u>RATE CONSTANT AT 298 K</u> ( $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ )
1. $e_{\text{aq}}^- + \text{H}^+ \rightarrow \cdot\text{H}$	$2.2 \times 10^{10}$
2. $\cdot\text{H} + \text{OH}^- \rightarrow \text{H}_2\text{O} + e_{\text{aq}}^-$	$2 \times 10^7$
3. $\text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^-$	$1 \times 10^8$
4. $\text{OH}^- + \text{HO}_2^- \rightarrow \text{H}_2\text{O} + \cdot\text{O}_2^-$	$1.6 \times 10^{-1}$
5. $e_{\text{aq}}^- + \text{H}_2\text{O} \rightarrow \cdot\text{H} + \text{OH}^-$	$2 \times 10^1$
6. $e_{\text{aq}}^- + e_{\text{aq}}^- + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + 2\text{OH}^-$	$5 \times 10^9$
7. $e_{\text{aq}}^- + \cdot\text{H} + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}_2$	$2.5 \times 10^{10}$
8. $e_{\text{aq}}^- + \text{HO}_2^- \rightarrow \text{OH}^- + \text{O}^-$	$3.5 \times 10^9$
9. $e_{\text{aq}}^- + \text{O}^- + \text{H}_2\text{O} \rightarrow 2\text{OH}^-$	$2 \times 10^{10}$
10. $e_{\text{aq}}^- + \cdot\text{O}_2^- \rightarrow \text{O}_2^-$	$1.3 \times 10^{10}$
11. $e_{\text{aq}}^- + \text{H}_2\text{O}_2 \rightarrow \text{OH}^- + \text{OH}^-$	$1.2 \times 10^{10}$
12. $e_{\text{aq}}^- + \text{HO}_2^- \rightarrow \text{HO}_2^-$	$2 \times 10^{10}$
13. $e_{\text{aq}}^- + \text{O}_2 \rightarrow \cdot\text{O}_2^-$	$2.0 \times 10^{10}$
14. $\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2$	$5.5 \times 10^9$
15. $\cdot\text{OH} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}^-$	$1.2 \times 10^{10}$
16. $e_{\text{aq}}^- + \cdot\text{OH} \rightarrow \text{OH}^-$	$3.0 \times 10^{10}$
17. $\cdot\text{H} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}$	$2 \times 10^{10}$
18. $\cdot\text{OH} + \text{HO}_2^- \rightarrow \text{OH}^- + \text{HO}_2^-$	$8.3 \times 10^9$
19. $\cdot\text{OH} + \cdot\text{O}_2^- \rightarrow \text{OH}^- + \text{O}_2$	$8 \times 10^9$
20. $\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}_2\text{O}$	$3 \times 10^7$
21. $\cdot\text{OH} + \text{HO}_2^- \rightarrow \text{H}_2\text{O} + \text{O}_2$	$1.4 \times 10^{10}$
22. $\cdot\text{OH} + \text{O}^- \rightarrow \text{HO}_2^-$	$1 \times 10^{10}$

...continued

TABLE B-1 (continued)

<u>REACTION</u>	<u>RATE CONSTANT AT 298 K</u> ( $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ )
23. $\cdot\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \cdot\text{H}$	$3.3 \times 10^7$
24. $\cdot\text{H} + \cdot\text{H} \rightarrow \text{H}_2$	$1 \times 10^{10}$
25. $\cdot\text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2$	$9 \times 10^7$
26. $\cdot\text{H} + \text{O} \cdot \rightarrow \text{OH} \cdot$	$2 \times 10^{10}$
27. $\cdot\text{H} + \cdot\text{O}_2 \rightarrow \text{HO}_2$	$2 \times 10^{10}$
28. $\cdot\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \cdot\text{OH}$	$7 \times 10^7$
29. $\cdot\text{H} + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2$	$2 \times 10^{10}$
30. $\cdot\text{H} + \text{O}_2 \rightarrow \text{HO}_2$	$2 \times 10^{10}$
31. $\text{HO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{OH} \cdot$	$1 \times 10^4$
32. $\text{HO}_2 + \text{O} \cdot \rightarrow \text{OH} \cdot + \cdot\text{O}_2$	$7 \times 10^8$
33. $\text{HO}_2 + \text{HO}_2 \rightarrow \text{OH} \cdot + \cdot\text{OH} + \text{O}_2$	1
34. $\text{O} \cdot + \text{O}_2 \rightarrow \text{O}_3$	$3 \times 10^9$
35. $\text{O} \cdot + \text{O}_3 \cdot \rightarrow \text{O}_2 + \text{O}_2$	$8 \times 10^8$
36. $\text{O} \cdot + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{OH} \cdot$	$1.7 \times 10^6$
37. $\text{O} \cdot + \text{H}_2 \rightarrow \cdot\text{H} + \text{OH} \cdot$	$8 \times 10^7$
38. $\text{O} \cdot + \text{O} \cdot \rightarrow \text{O}_2$	$1 \times 10^9$
39. $\text{O} \cdot + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \cdot\text{O}_2$	$8 \times 10^9$
40. $\cdot\text{O}_2 + \cdot\text{O}_2 \rightarrow \text{O}_2 + \text{O}_2$	$1.7 \times 10^7$
41. $\cdot\text{O}_2 + \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \text{OH} \cdot + \text{O}_2$	1
42. $\cdot\text{O}_2 + \text{HO}_2 \rightarrow \text{HO}_2 + \text{O}_2$	$7 \times 10^7$
43. $\text{HO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + \text{H}_2\text{O} + \cdot\text{OH}$	1
44. $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$2 \times 10^6$
45. $\text{H}^+ + \text{OH} \cdot \rightarrow \text{H}_2\text{O}$	$1.43 \times 10^{11}$
46. $\text{H}^+ + \text{O} \cdot \rightarrow \cdot\text{OH}$	$5 \times 10^{10}$
47. $\cdot\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{HO}_2 + \text{OH} \cdot$	$1 \times 10^4$
48. $\text{H}^+ + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2$	$5 \times 10^{10}$
49. $\text{H}^+ + \cdot\text{O}_2 \rightarrow \text{HO}_2$	$5 \times 10^{10}$
50. $\cdot\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{HO}_2 + \text{OH} \cdot$	$1 \times 10^4$

... continued

TABLE B-1 (concluded)

<u>REACTION</u>	<u>RATE CONSTANT AT 298 K</u> ( $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ )
51. $\text{H}^+ + \cdot\text{O}_2^- \rightarrow \text{HO}_2$	$5 \times 10^{10}$
52. $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$	$2.6 \times 10^{-5}$
53. $\text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{HO}_2$	$1 \times 10^{-1}$
54. $\text{HO}_2 \rightarrow \text{H}^+ + \cdot\text{O}_2^-$	$8 \times 10^5$
55. $\cdot\text{OH} \rightarrow \text{H}^+ + \text{O}^-$	$1 \times 10^{-1}$

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