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Effect of Irradiation Dose and Storage Time on the Free Radical Concentrations in Gamma-Irradiated Dried Seasoning Powder

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Abstract

Electron spin resonance (ESR) spectroscopy was used to investigate the effect of irradiation dose and storage time on the free radical concentrations in gamma-irradiated dried seasoning powder. Seasoning powders of dried squid flavor, shrimp flavor, *kimchi* flavor, spicy beef soup flavor and soy sauce flavor were irradiated with doses of 0, 1, 3, 5, 7 and 9 kGy at room temperature using a Co-60 irradiator. Characteristic signals of free radicals were observed in all the irradiated samples of this experiment, while these signals were not detected in non-irradiated samples. Since the free radical concentrations linearly increased with the applied doses (1~9 kGy), highly positive correlation coefficients (R^2 = 0.9285~0.9965) were obtained between irradiation doses and free radical concentrations during all the storage times. Free radical concentrations of the irradiated *kimchi* flavored seasoning powder did not change even at 16 weeks of storage at room temperature, while those of dried squid, shrimp and spicy beef soup flavors decreased until 2 weeks of storage after irradiation with 5 kGy or over, and those of soy sause flavors slowly decreased until 8 weeks of storage after irradiation with 3 kGy or over. Although the free radical concentrations decreased with storage times, the characteristic signals of the irradiated seasoning powders of dried squid, shrimp, spicy beef and soy sauce flavors were observed even after 16 weeks of storage at room temperature.

Key words: ESR spectroscopy, irradiated dried seasoning powder, free radical concentrations

INTRODUCTION

One of the biggest problems of dried powdered seasoning spices and their ingredients is that they spoil easily due to the growth of microorganisms during distribution and storage. Irradiation techniques have increased the possibilities of solving the microbial problem. The traditional methods for pasteurization of complex foods of seasoning were heating, UV, microwave and chemical fumigants. The heating method has a limited usage because it has problems of nutritional loss, physical changes of texture, flavor changes or secondary contamination. Treatments using UV and microwaves have the problem of limiting pasteurization to the food surface. Particularly, chemical fumigants used frequently in commercial products have been forbidden or limited by concern about the residue in food and environmental pollution (1).

Concern about irradiation for food quality gradually increased because irradiation is a new technology which gives safety without changing the flavor and other characteristics. Actually, irradiation of 1 kGy or 10 kGy was permitted to control the growth of microorganisms over 9 countries including the USA, England and Korea. Nowadays, irradiation application to food is commercially used in approximately 30 countries. Each country is forced to regulate the irradiation and to label the irradiation amount because consumers do not have enough knowledge on the safety of irradiated foods and because they do not intend to use irradiated foods. Therefore, it should be known to consumers whether they are taking foods irradiated with appropriate regulations or not. At the same time, a practical detection method to distinguish between irradiated foods and non-irradiated ones was seriously needed for the acceleration and establishment of international trade.

While detection methods of dried seasoning powders on irradiation were little studied in foreign countries, it was studied by several researchers in Korea (2,3). The analysis with TL reaction depends on inorganic materials in food. The reason why it analyzes the separated inorganic materials rather than total samples is because the degree of mixing of inorganic materials is different according to harvesting area, and treatment method of the harvest samples. However, the disadvantages of this method are that it takes long time and requires a lot of samples (4). In

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the other side, electron spin resonance (ESR) spectroscopy can measure ions and free radicals which were produced from the broken molecular bonds by the partial energy of irradiation. It is known to be a non-destructive detection method of simple and fast sample preparation compared with other methods (5,6). Despite of several advantages, little research of dried-seasoning powders on irradiation effects by using ESR spectroscopy has been conducted.

The objectives of this study were to know the relationship between the irradiated amounts and the amounts of the formed free radicals by ESR spectroscopy during storage of the dried seasoning powders which are used as an ingredient of lameon soup, and to provide the useful basic data for deciding the irradiated amounts of dried seasoning powders as well as to know whether dried seasoning powders were treated by irradiation or not.

MATERIALS AND METHODS

Sample preparation

The seasoning powders used in this study were flavored dried squid, shrimp, *kimchi*, spicy beef and soy sauce. They were obtained from Korean food companies. The samples were packed in polyethylene bag (50 g) of 10 × 10 cm. The packed samples were irradiated using a Co-60 irradiator (AECL IR-79, Canada) with doses of 0, 1, 3, 5, 7 and 9 kGy at room temperature and the rates for Co-60 sources were determined by using a ceric cerous dosimeter.

ESR measurement

Electron spin resonance (ESR) was measured by ESR X-band spectrometer (Bruker EPR 300 spectrometer, Bruker Instruments Inc., Germany). One hundred milligrams of three samples of each seasoning powder in every irradiation were measured to be put into ESR quartz tube of 4 mm (i.d). The tubes were placed in the resonator located between positive and negative of the electromagnet, to provide the sufficient magnetic field within the spectrometer. It was measured until the energy absorption from the magnetic field in a microwave was constant. The amounts of free radicals formed from the irradiated samples for 18 weeks at room temperature were measured by ESR signals.

ESR spectrometer settings were magnetic center field of 3460 G, microwave frequency of 9.73 GHz, microwave power of 5.029 mW, time constant of signal channel of 0.640 ms, sweep time of 10.486 s, receiver gain of 1.0×10^4, modulation amplitude of 3.0 G and modulation frequency of 100 kHz at 23°C.

Analysis of results

ESR results were obtained by Bruker Win-EPR with the software program of Simponia, and the concentration of free radicals was quantified by measuring the primary differentiation of the absorbed curve intensities of ESR signal on the peak areas of the applied magnetic field. Triplicates on each sample in every irradiation were shown by mean ± standard deviation.

RESULTS AND DISCUSSION

ESR spectra and free radical concentration on irradiation

ESR spectra of non-irradiated and 7 kGy irradiated samples are shown in Fig. 1a and Fig. 1b, respectively. The peaks of ESR spectra of non-irradiated samples were not detected showing no free radicals, while irradiated samples were observed by signals of characteristic free radicals. The values were g_1=2.0057 ± 0.00006 for squid taste, g_1=2.0177 ± 0.00008, g_2=2.0087 ± 0.00008, g_3=2.0024 ± 0.00009, g_4=1.9970 ± 0.00009 for *kimchi* flavoring, g_1= 2.0058 ± 0.00010 for spicy beef flavoring. ESR spectras of squid and spicy beef flavored seasoning powder were the same shapes of singlet line, but that of *kimchi* flavoring was a multiple type. Soups of shrimp flavoring and soy source flavoring showed Mn^{2+} peaks with 6 similar distances in both irradiated and non-irradiated samples. These results were similar to other reports of Nam et al. (7) on crab and Stewart et al. (8) on scampi. Irradiated samples showed the difference from non-irradiated samples, showing g_1=2.0189 ± 0.00016, g_2=2.0053 ± 0.00007, g_3=1.9890 ± 0.00011 for the soup of shrimp flavoring, g_1=2.0052 ± 0.00010 for the soup of soy source flavoring.

Radical concentrations on the amount of irradiation to dried seasoning powders are shown in Fig. 2. The free radical concentration was known to be linearly increased with the applied dose (1~9 kGy). As shown from the regressions of Table 1, the relationships between the radical concentration (y) and the amount of irradiation (x) were $y=(3.07x+0.89) \times 10^6$ for squid flavoring, $y=(2.05x+1.09) \times 10^6$ for shrimp flavoring soup, $y=(3.44x+0.17) \times 10^6$ for *kimchi* flavoring, $y=(2.47x+1.01) \times 10^6$ for spicy beef flavoring, $y=(9.96x+19.25) \times 10^5$ for soy source flavoring. Correlation cofficients (R^2) between the amount of irradiation and the formation of radicals were highly positive, having the range of 0.9681~0.9958 (Table 1). The R^2s were 0.9607 to 0.9965 for 2 weeks, 0.9585 to 0.9937 for 4 weeks, 0.9846 to 0.9913 for 8 weeks, 0.9780 to 0.9958 for 13 weeks, 0.9635 to 0.9907 for 15 weeks, 0.9285 to 0.9912 for 18 weeks. Therefore, R^2 of all samples had the high values within the range from 0.9285 to 0.9965. Chung and Kwon (3) reported that R^2 between irradiation and TL response in detection method of seasoning powder using TL was more than 0.5966. In this

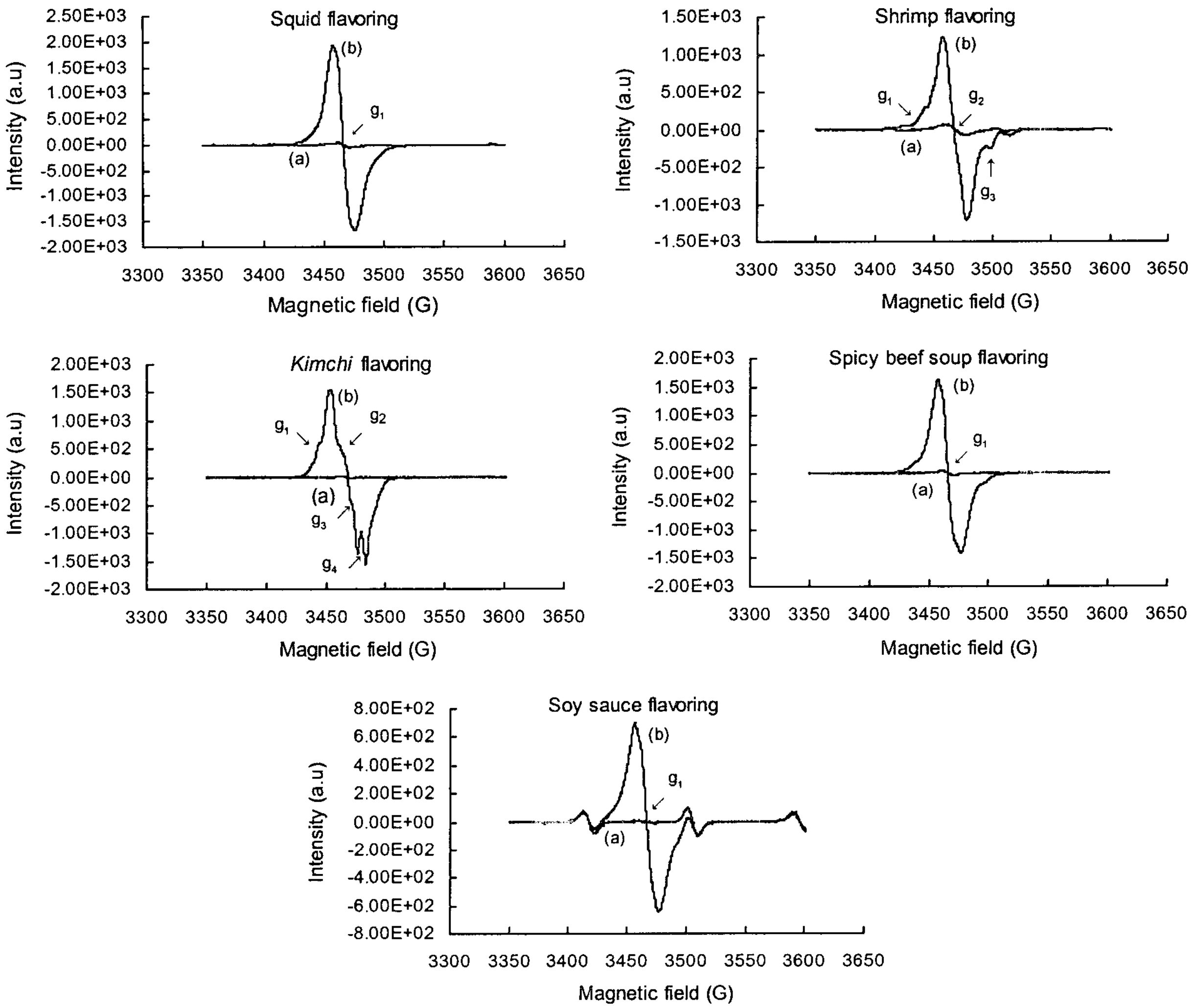

Fig. 1. Characteristic ESR spectrum derived from non-irradiated (a) and irradiated dried seasoning powder at 7 kGy (b).

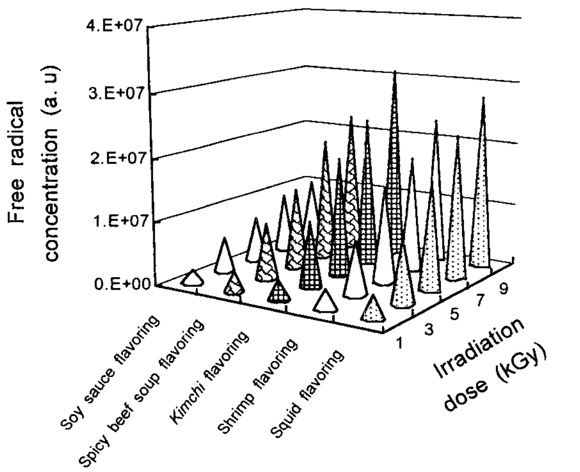

Fig. 2. Dose-dependent free radical concentration in irradiated dried seasoning powder.

study of using ESR spectroscopy, R^2 between the amount of irradiation and ESR signal was more than 0.9285 for all samples of 18 weeks. It was certain that ESR spectroscopy in measuring the formation of free radicals of irradiated samples had more potential for better analysis than the TC method.

Changes of free radical concentration during storage time

Changes of the amounts of free radicals during storage of samples are shown in Fig. 3. The sizes of signals between the soup of *kimchi*-flavored powder stored for 18 weeks after irradiation and the just irradiated soup were little changed for all the applied doses (1~9 kGy). The sizes of the signals of the irradiated soups of squid flavoring, shrimp flavoring and spicy beef flavoring with 5 kGy or over were decreased for 2 weeks. And no significant change was not detected after 2 weeks in irradiated soups of squid, shrimp and spicy beef flavoring. Those of the irradiated soups of soy source flavoring with 3 kGy or over were slowly decreased for 8 weeks. Then, no significant change was detected in irradiated soups of soy sauce flavoring. Radical concentrations in the high dose-

Table 1. Linear regression between irradiation doses and free radical concentrations of irradiated dried seasoning powder

Storage time (week)	Squid flavoring		Shrimp flavoring		*Kimchi* flavoring		Spicy beef soup flavoring		Soy sauce flavoring	
	Regression equation[1)]	R^2[2)]	Regression equation	R^2	Regression equation	R^2	Regression equation	R^2	Regression equation	R^2
0	$y=(3.07x+0.89)\times10^6$	0.9958	$y=(2.50x+1.09)\times10^6$	0.9888	$y=(3.44x+0.17)\times10^6$	0.9945	$y=(2.48x+1.01)\times10^6$	0.9893	$y=(9.95x+19.2)\times10^5$	0.9681
2	$y=(2.57x+0.93)\times10^6$	0.9933	$y=(2.04x+0.77)\times10^6$	0.9965	$y=(3.50x+1.01)\times10^6$	0.9934	$y=(2.01x+0.89)\times10^6$	0.9925	$y=(7.11x+18.7)\times10^5$	0.9607
4	$y=(2.34x+1.05)\times10^6$	0.9916	$y=(1.88x+0.81)\times10^6$	0.9937	$y=(3.41x+1.09)\times10^6$	0.9916	$y=(1.80x+0.84)\times10^6$	0.9936	$y=(6.04x+17.9)\times10^5$	0.9585
8	$y=(2.13x+1.07)\times10^6$	0.9906	$y=(1.75x+0.96)\times10^6$	0.9909	$y=(3.39x+1.23)\times10^6$	0.9914	$y=(1.55x+0.89)\times10^6$	0.9902	$y=(4.73x+14.8)\times10^5$	0.9727
10	$y=(1.99x+1.10)\times10^6$	0.9913	$y=(1.63x+0.83)\times10^6$	0.9878	$y=(3.31x+1.15)\times10^6$	0.9899	$y=(1.48x+0.74)\times10^6$	0.9904	$y=(4.33x+12.9)\times10^5$	0.9846
13	$y=(1.90x+1.12)\times10^6$	0.9888	$y=(1.54x+0.80)\times10^6$	0.9958	$y=(3.40x+1.20)\times10^6$	0.9903	$y=(1.43x+0.69)\times10^6$	0.9920	$y=(4.02x+12.4)\times10^5$	0.9780
15	$y=(1.77x+1.06)\times10^6$	0.9891	$y=(1.44x+0.91)\times10^6$	0.9852	$y=(3.25x+1.25)\times10^6$	0.9907	$y=(1.26x+0.95)\times10^6$	0.9824	$y=(3.64x+10.6)\times10^5$	0.9635
18	$y=(1.62x+1.08)\times10^6$	0.9895	$y=(1.39x+0.81)\times10^6$	0.9912	$y=(3.14x+1.06)\times10^6$	0.9900	$y=(1.19x+0.58)\times10^6$	0.9863	$y=(3.72x+0.75)\times10^5$	0.9285

1)x = irradiation dose, y = free radical concentration.
2)R^2 = correlation between irradiation doses and free radical concentrations.

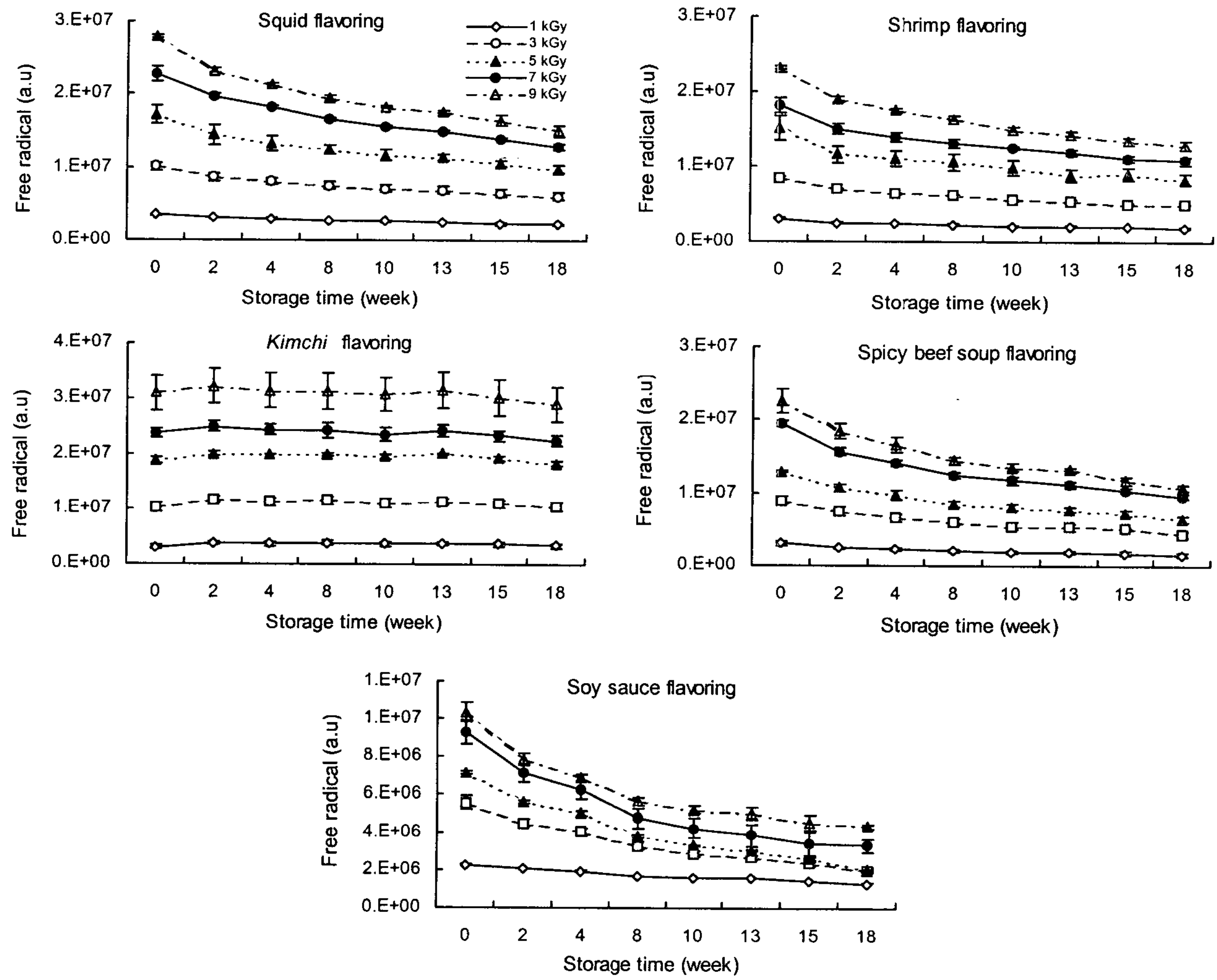

Fig. 3. Changes of free radical concentration of dried seasoning powder during storage period at room temperature.

irradiated samples were decreased more rapidly than those in low dose-irradiated samples. To compare the 18 week-stored samples with the just irradiated samples, the regression formulas between the radicals concentration of the stored samples and the amount of doses for irradiation are shown in Table 1. The soup of squid flavoring was decreased from $y=(3.07x+0.89)\times10^6$ to $y=(1.62x+1.08)\times10^6$. Shrimp-flavored soup was from $y=(2.05x+1.09)\times10^6$ to $y=(1.39x+0.81)\times10^6$, while *kimchi*-flavored soup was little changed from $y=(3.44x+0.17)\times10^6$ to $y=(3.14x+1.06)\times10^6$. The soup of spicy beef flavoring was changed from $y=(2.47x+1.01)\times10^6$ to $y=(1.19x+0.58)\times10^6$. The soup of soy source flavoring was from $y=(9.96x+19.25)\times10^5$ to $y=(3.72x+0.75)\times10^5$.

Table 2. Linear regression between storage time and free radical concentration of irradiated dried seasoning powder

	Squid flavoring		Shrimp flavoring		*Kimchi* flavoring		Spicy beef soup flavoring		Soy sauce flavoring	
Dose	Regression equation[1)]	R^2	Regression equation	R^2	Regression equation	R^2	Regression equation	R^2	Regression equation	R^2
1 kGy	$y=3.56x^{-0.210}\times 10^6$	0.9790	$y=2.99x^{-0.217}\times 10^6$	0.9743	$y=3.39x^{-0.056}\times 10^6$	0.3009	$y=3.11x^{-0.311}\times 10^6$	0.9640	$y=2.37x^{-0.249}\times 10^6$	0.9386
3 kGy	$y=1.02x^{-0.230}\times 10^7$	0.9832	$y=8.45x^{-0.250}\times 10^6$	0.9883	$y=1.10x^{0.009}\times 10^7$	0.0255	$y=9.17x^{-0.318}\times 10^6$	0.9744	$y=6.10x^{-0.476}\times 10^6$	0.9457
5 kGy	$y=1.73x^{-0.251}\times 10^7$	0.9827	$y=1.48x^{-0.264}\times 10^7$	0.9693	$y=1.95x^{-0.002}\times 10^7$	0.0039	$y=1.33x^{-0.318}\times 10^7$	0.9796	$y=8.06x^{-0.568}\times 10^6$	0.9346
7 kGy	$y=2.35x^{-0.267}\times 10^7$	0.9738	$y=1.81x^{-0.242}\times 10^7$	0.9923	$y=2.45x^{-0.021}\times 10^7$	0.2201	$y=1.97x^{-0.329}\times 10^7$	0.9916	$y=9.86x^{-0.516}\times 10^6$	0.9797
9 kGy	$y=2.84x^{-0.282}\times 10^7$	0.9862	$y=2.33x^{-0.277}\times 10^7$	0.9927	$y=3.19x^{-0.023}\times 10^7$	0.2705	$y=2.32x^{-0.342}\times 10^7$	0.9815	$y=1.05x^{-0.422}\times 10^7$	0.9938

[1)]x = storage time, y=free radical concentration.

Regression formular between the concentration of free radicals (y) and the storage time (x) were obtained from the samples irradiated with 7 kGy of the commercial doses. The squid-flavored soup was $y=2.35x^{-0.267}\times 10^7$ (R^2= 0.9738), shrimp flavoring was $y=1.81x^{-0.242}\times 10^7$ (R^2= 0.9923), *kimchi* flavoring was $y=2.45x^{-0.021}\times 10^7$ (R^2= 0.2201), spicy beef flavoring was $y=1.97x^{-0.329}\times 10^7$ (R^2= 0.9916), and soy source flavoring was $y=9.86x^{-0.516}\times 10^6$ (R^2= 0.9797) (Table 2). Especially, R^2 between free radical concentration of the *kimchi*-flavored soup and its storage time was 0.2201, and the free radical concentration formed by irradiation was little changed during storage. These results of ESR spectroscopy can be helpful to determine whether any dried seasoning powders stored for 18 weeks were treated by irradiation or not. Also, it would be possible to estimate the amount of irradiation on each sample stored.

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