

Supplementary Material

Physico-Chemical Changes Induced by Gamma Irradiation on Some Structural Protein Extracts

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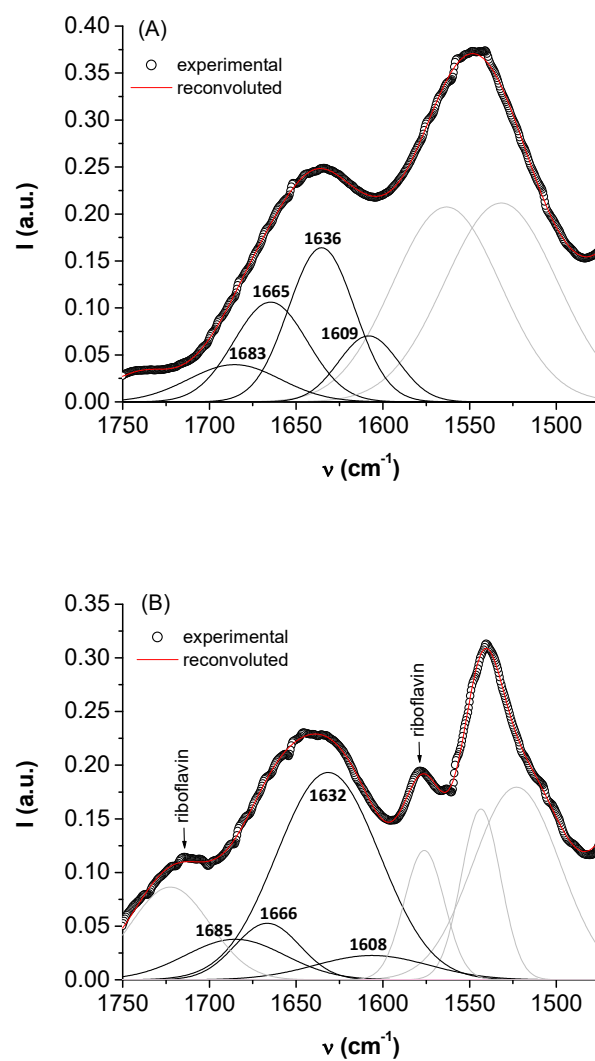


Figure S1. Deconvolution of the amide I region of the IR spectra of (A) collagen, (B) collagen/riboflavin/irradiated; for clarity, band components not belonging to the region of interest are depicted in grey.

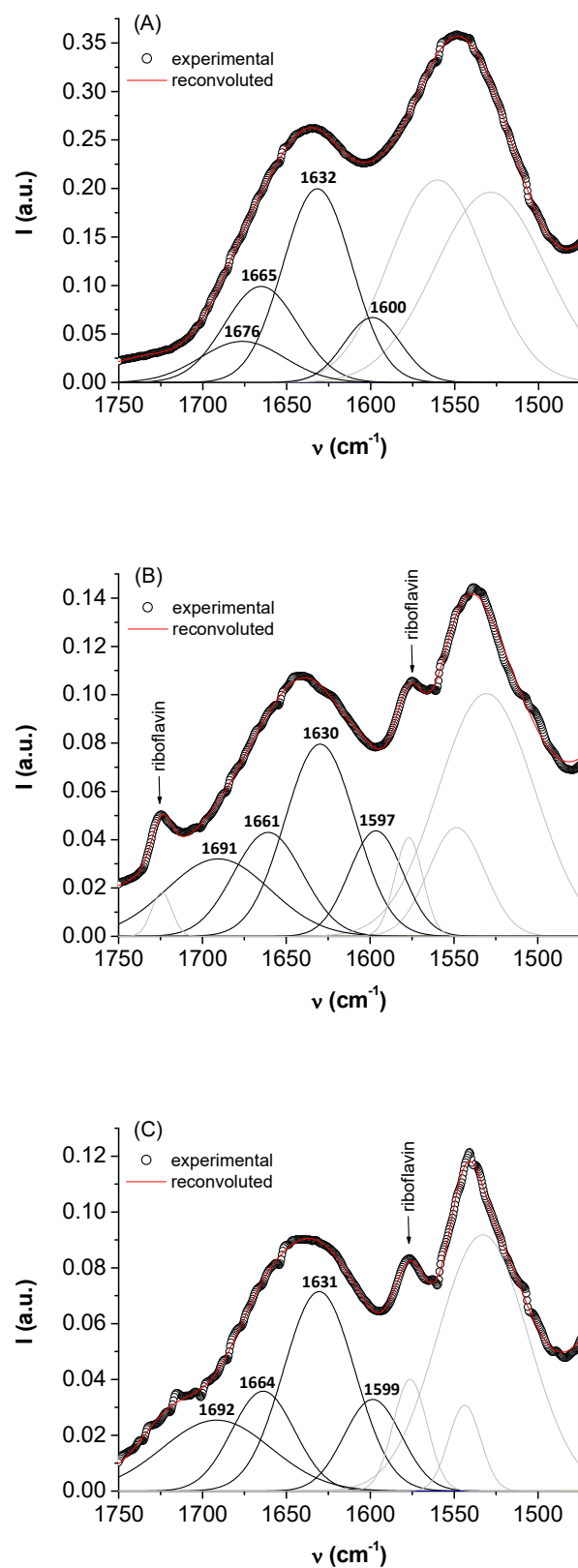


Figure S2. Deconvolution of the amide I region of the IR spectra of (A) bovine gelatin, (B) bovine gelatin/riboflavin, (C) bovine gelatin/riboflavin/gamma irradiated; for clarity, band components not belonging to the region of interest are depicted in grey.

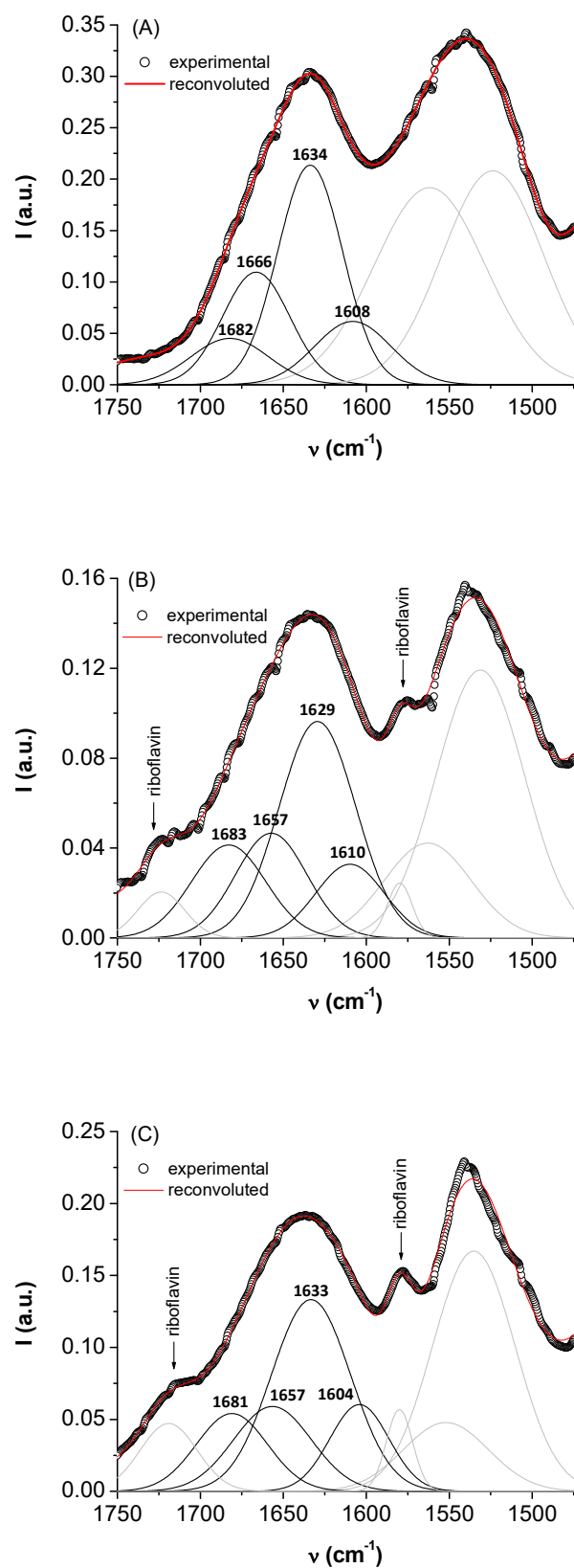


Figure S3. Deconvolution of the amide I region of the IR spectra of (A) fish gelatin, (B) fish gelatin/riboflavin, (C) fish gelatin/riboflavin gamma irradiated; for clarity, band components not belonging to the region of interest are depicted in grey.

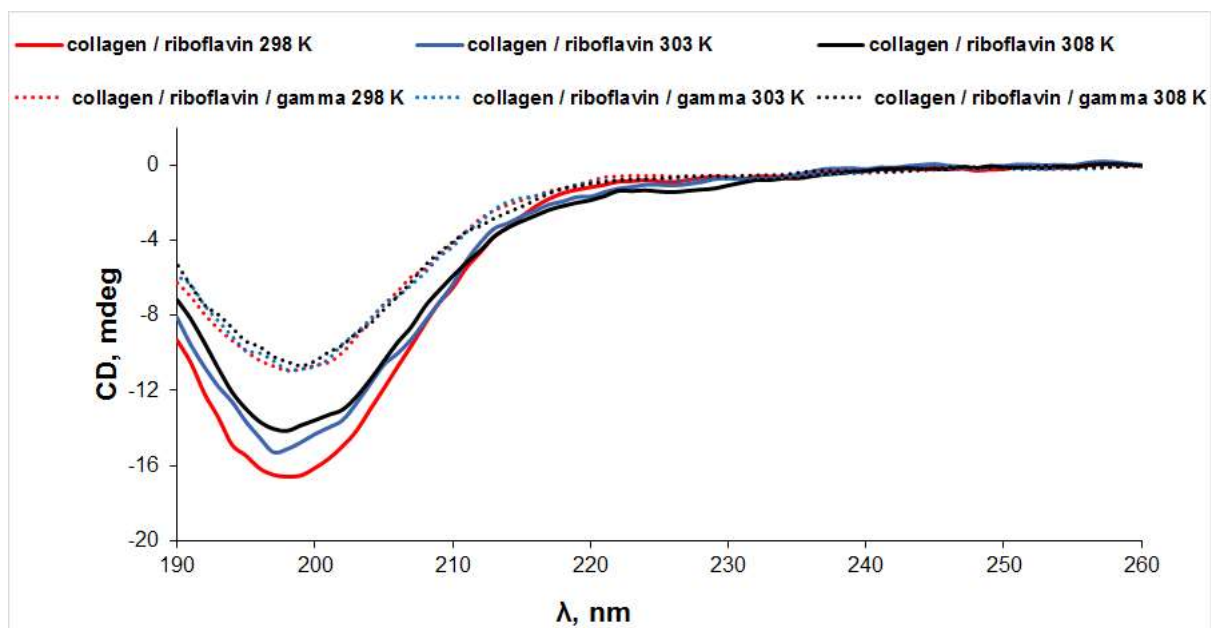


Figure S4. The CD spectra of collagen/riboflavin (line) and collagen/riboflavin/gamma irradiated (dotted line) solutions in acetic acid 0.18 M at different temperatures.

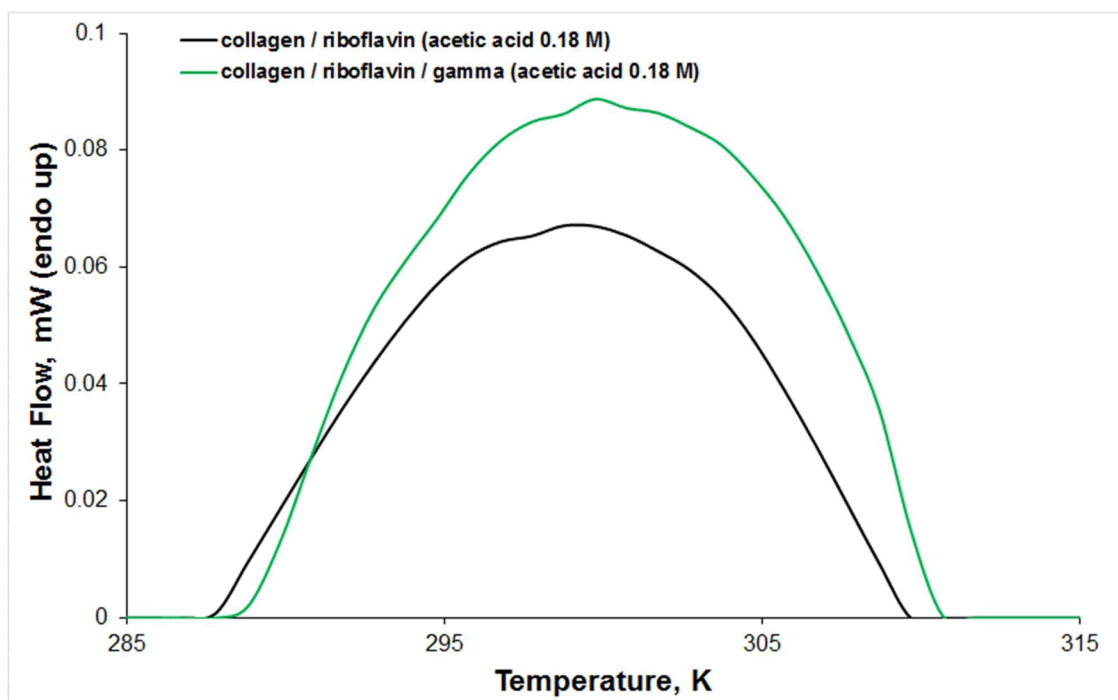


Figure S5. The μ DSC signal for the thermal denaturation of collagen/riboflavin solution in acetic acid 0.18 M, prior to and after gamma irradiation.

Table S1. Assignment of the main IR bands of collagen.

Sample	Wavenumber (cm ⁻¹)	Assignment
collagen	3290, 3076 (w)	O-H, N-H stretching (amide A and B)
	2958 (w), 2923, 2873 (w), 2852	C-H stretching (asymmetric, symmetric)
	1636 (s)	C=O stretching/N-H bending (amide I)
	1547 (s)	C-N stretching/N-H bending (amide II)
	1446, 1408 (s)	C-H bending
	1344, 1242	C-N stretching/N-H bending (amide III)
	1080, 1050, 1020	C-O stretching (glycated collagen)
collagen/riboflavin	3300, 3072 (w)	O-H, N-H stretching (amide A and B)
	2927, 2854	C-H stretching (asymmetric, symmetric)
	1645 (w)	C=O stretching/N-H bending (amide I)
	1538 (s)	C-N stretching/N-H bending (amide II)
	1445, 1407 (s)	C-H bending
	1343, 1240	C-N stretching/N-H bending (amide III)
	1086, 1052, 1021	C-O stretching (glycated collagen)
collagen/riboflavin/gamma	3290, 3069	O-H, N-H stretching (amide A and B)
	2954, 2919 (s), 2972, 2851 (s)	C-H stretching (asymmetric, symmetric)
	1642 (s)	C=O stretching/N-H bending (amide I)
	1540 (s)	C-N stretching/N-H bending (amide II)
	1404 (w)	C-H bending
	1245	C-N stretching/N-H bending (amide III)
	1077, 1060, 1028	C-O stretching (glycated collagen)

Abbreviations: s – strong, w – weak.

Table S2. Assignment of the main IR bands of bovine gelatin.

Sample	Wavenumber (cm ⁻¹)	Assignment
bovine gelatin	3300, 3071	O-H, N-H stretching (amide A and B)
	2960 (w), 2928, 2875 (w), 2851 (w)	C-H stretching (asymmetric, symmetric)
	1635 (s)	C=O stretching/N-H bending (amide I)
	1549 (s)	C-N stretching/N-H bending (amide II)
	1448 (w), 1409	C-H bending
	1343, 1243	C-N stretching/N-H bending (amide III)
	1080, 1050, 1021	C-O stretching (glycated gelatin)
bovine gelatin/riboflavin	3276, 3069	O-H, N-H stretching (amide A and B)
	2931 (w), 2876 (w)	C-H stretching (asymmetric, symmetric)
	1642 (s)	C=O stretching/N-H bending (amide I)
	1538 (s)	C-N stretching/N-H bending (amide II)
	1454 (w), 1409	C-H bending
	1343, 1251	C-N stretching/N-H bending (amide III)
	1081; 1021	C-O stretching (glycated gelatin)
bovine gelatin/riboflavin/gamma	3300, 3068	O-H, N-H stretching (amide A and B)
	2955 (w), 2918 (s), 2873 (w), 2849 (s)	C-H stretching (asymmetric, symmetric)
	1638 (s)	C=O stretching/N-H bending (amide I)
	1541 (s)	C-N stretching/N-H bending (amide II)
	1448 (w), 1404 (w)	C-H bending
	1350; 1246	C-N stretching/N-H bending (amide III)
	1061, 1031	C-O stretching (glycated gelatin)

Abbreviations: s – strong, w – weak.

Table S3. Assignment of the main IR bands of fish gelatin.

Sample	Wavenumber (cm ⁻¹)	Assignment
fish gelatin	3275, 3076	O-H, N-H stretching (amide A and B)
	2960 (w), 2933, 2877 (w), 2852 (w)	C-H stretching (asymmetric, symmetric)
	1635 (s)	C=O stretching/N-H bending (amide I)
	1540 (s)	C-N stretching/N-H bending (amide II)
	1446, 1406 (s)	C-H bending
	1338, 1243	C-N stretching/N-H bending (amide III)
	1080, 1050, 1024	C-O stretching (glycated gelatin)
fish gelatin/riboflavin	3279, 3070	O-H, N-H stretching (amide A and B)
	2934, 2877 (w)	C-H stretching (asymmetric, symmetric)
	1634 (s)	C=O stretching/N-H bending (amide I)
	1538 (s)	C-N stretching/N-H bending (amide II)
	1452, 1401	C-H bending
	1343, 1247	C-N stretching/N-H bending (amide III)
	1079, 1061, 1029	C-O stretching (glycated gelatin)
fish gelatin/riboflavin/gamma	3283, 3068	O-H, N-H stretching (amide A and B)
	2955, 2918 (s), 2872, 2851 (s)	C-H stretching (asymmetric, symmetric)
	1638 (s)	C=O stretching/N-H bending (amide I)
	1539 (s)	C-N stretching/N-H bending (amide II)
	1444, 1403	C-H bending
	1347, 1245	C-N stretching/N-H bending (amide III)
	1077, 1057, 1028	C-O stretching (glycated gelatin)

Abbreviations: s – strong, w – weak.

Table S4. Secondary structure content of collagen samples.

Sample	Band Assignment	ν (cm ⁻¹)	% Area
collagen	β -sheet	1609	15
	random coil	1636	41
	α -helix	1665	30
	β -turn	1683	14
collagen/riboflavin/gamma	β -sheet	1608	8
	random coil	1632	68
	α -helix	1666	12
	β -turn	1685	12

Table S5. Secondary structure content of bovine gelatin samples.

Sample	Band Assignment	ν (cm ⁻¹)	% Area
bovine gelatin	β -sheet	1600	13
	random coil	1632	48
	α -helix	1665	26
	β -turn	1676	13
bovine gelatin/riboflavin	β -sheet	1597	17
	random coil	1630	40
	α -helix	1661	21
	β -turn	1691	22
bovine gelatin/riboflavin/gamma	β -sheet	1599	16
	random coil	1631	43
	α -helix	1664	19
	β -turn	1692	23

Table S6. Secondary structure content of fish gelatin samples.

Sample	Band Assignment	ν (cm ⁻¹)	% Area
fish gelatin	β -sheet	1608	16
	random coil	1634	47
	α -helix	1666	25
	β -turn	1682	12
fish gelatin/riboflavin	β -sheet	1610	14
	random coil	1629	46
	α -helix	1657	21
	β -turn	1683	19
fish gelatin/riboflavin/gamma	β -sheet	1604	16
	random coil	1633	47
	α -helix	1657	20
	β -turn	1681	17

Table S7. Peak temperature and denaturation enthalpy change obtained from μ DSC measurements for solutions prepared in acetic acid 15.7 M.

Sample	T_{peak} (K)	ΔH (J/g)
keratin	300.75	1.12
keratin/riboflavin/gamma	300.79	0.95
collagen	303.84	2.56
collagen/riboflavin/gamma	298.07	0.21
bovine gelatin	302.64	2.43
bovine gelatin/riboflavin/gamma	301.45	1.19
fish gelatin	303.64	2.14
fish gelatin/riboflavin/gamma	303.14	0.75

Table S8. Parameters of the DMPO and PBN spin adducts formed in protein/riboflavin solutions after exposure to gamma radiation.

Sample	DMPO				PBN			
	1 hour		2 hours		1 hour		2 hours	
	a_N (G)	a_H (G)	a_N (G)	a_H (G)	a_N (G)	a_H (G)	a_N (G)	a_H (G)
keratin	-	-	15.00	14.73	-	-	-	-
collagen	14.80	13.97	14.80	14.04	14.70	2.76	14.85	3.15
bovine gelatin	14.75	13.86	14.75	13.90	14.61	2.56	14.75	2.95
fish gelatin	14.70	13.80	14.75	13.95	14.55	2.50	14.65	2.60