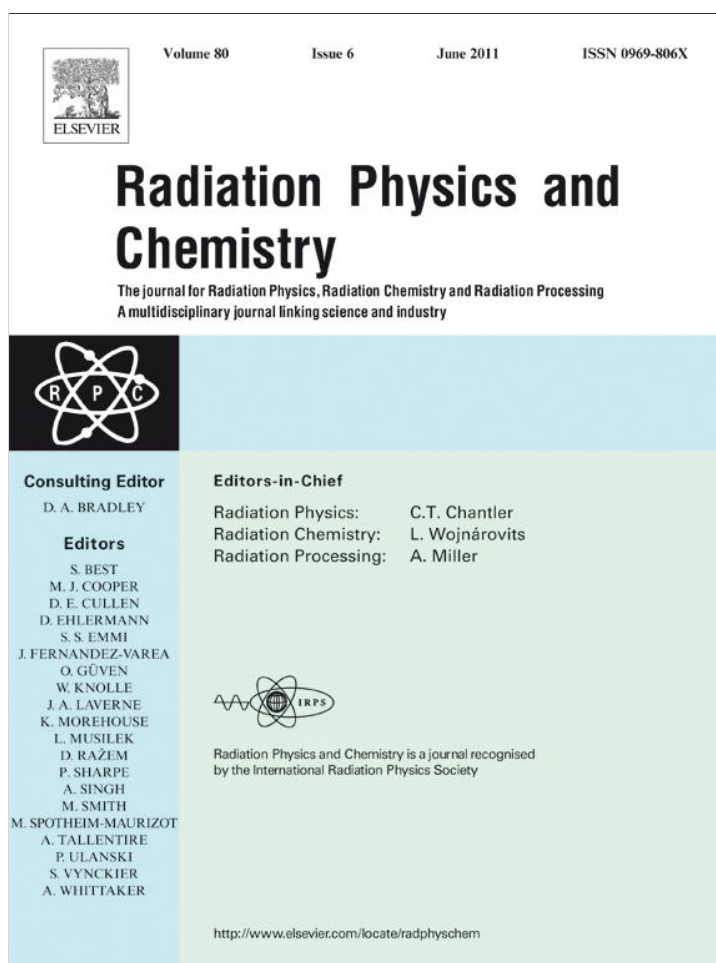


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Radical kinetics and dosimetric features of gamma-irradiated disodium ethylenediaminetetraacetic acid

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ABSTRACT

Dosimetric potential and kinetic features of disodium ethylenediaminetetraacetic acid (NaEDTA) were explored through a detail electron spin resonance (ESR) study performed at various temperatures on samples irradiated at various radiation doses. Irradiated NaEDTA was observed to exhibit an unresolved ESR spectrum consisting of many intense and weak resonance lines spread over a magnetic field range of about 7 mT and centered at $g=2.00275$. Findings derived from applied microwave power, long term storage investigation, and high and low temperature studies indicate that two radicals were formed after the irradiations. The spectroscopic parameters of these radicals were determined through spectrum simulation calculations. The dosimetric potential of NaEDTA was also investigated and it was concluded that NaEDTA does not present the characteristics of a good dosimetric material, but that ESR spectroscopy could be used in the discrimination of irradiated NaEDTA from the unirradiated one even long after irradiation. Activation energies of the involved species were also determined using the data derived from annealing studies performed at high temperatures.

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1. Introduction

Disodium ethylenediaminetetraacetic acid dihydrate (NaEDTA) or chemically disodium *N,N*-1,2-ethanediylibis[*N*-(carboxymethyl)glycine] is a sodium salt of EDTA. NaEDTA is water soluble odorless white crystalline powder with melting point of about 510–518 K. EDTA crystallizes as the monoclinic with space group $C2/c$ and there are four molecules in the unit cell (Ladd and Povey, 1973a, 1973b; Ladd et al., 1974). It is widely used in textile, pulp and paper, food and cosmetic industry and also in medicine (Welcher, 1961; Flaschka, 1964; Furia, 1964; DeBusk, 2002; Lanigan and Yamarik, 2002; Oviedo and Rodriguez, 2003). Its usefulness arises because of its role as a chelating agent, i.e. its ability to sequester metal ions such as Ca^{2+} , Mn^{2+} and Fe^{3+} .

Electron spin resonance (ESR) is a very suitable technique for the investigation of characteristics of the radical species produced in samples after irradiation and radiation dose determinations (Tuner and Korkmaz, 2007, 2009; Ustundag and Korkmaz, 2009). Effects of gamma radiation on single crystal of EDTA have already been reported in a previous short work (Köksal and Osmanoglu, 1993). It is proposed that $\dot{C}H_2CH_2N(CH_2CO_2H)_2$ and $CH_3\dot{C}OOH$ were the radicals produced after gamma-irradiated single crystals of diethylenediaminepentaacetic acid (DTPA) and ethylenediaminetetraacetic acid (EDTA), respectively (Köksal and Osmanoglu,

1993). However, no attempt has been made to determine the kinetic features of the produced radicals and possible dosimetric potential of NaEDTA.

The aim of the present work is to determine room (290 K) and high temperature (370, 380, 390 and 400 K) kinetics of the radicals produced in gamma-irradiated NaEDTA and to explore the radiosensitivity of gamma-irradiated NaEDTA through annealing studies and dosimetric investigations using ESR spectroscopy.

2. Materials and methods

White polycrystalline NaEDTA dihydrate samples were provided from GMT Food Ingredients Company (Istanbul) and stored at room temperature in a well closed container protected from light and change of humidity. No further purification was performed. All irradiations were performed at room temperature (290 K) using ^{60}Co - γ source supplying a dose rate of 1.41 kGy/h. The dose rate at the sample site was measured by a Fricke dosimeter. Investigations were performed on samples irradiated in the dose range of 1–34 kGy. A set of samples irradiated to doses 1, 2, 3, 5, 7, 10, 15, 25 and 34 kGy was employed to construct the dose–response curves. Samples irradiated to a dose of 10 kGy were used to investigate room and high temperature stability and decay kinetics of the radiation-induced radicals. Annealing studies were performed at four different temperatures (370, 380, 390 and 400 K) by heating samples inside ESR microwave cavity to

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Table 1
Spectrometer operation conditions adopted during the experiments.

	Room and high temperatures	Low temperature
Central field (mT)	350.5	335.5
Scan range (mT)	12	12
Microwave power (mW)	0.4	0.004
Microwave frequency (GHz)	9.85	9.42
Receiver gain ($\times 10^3$)	2.52	5.04
Modulation frequency (kHz)	100	100
Modulation amplitude (mT)	0.1	0.1
Time constant (ms)	327.68	327.68
Sweep time (s)	83.89	83.89

avoid any drawback originating from sample positioning in the microwave cavity.

ESR measurements were carried out on samples in standard ESR quartz tubes of 4 mm inner diameter using a Bruker EMX-131 X-band ESR spectrometer operating at 9.8 GHz and equipped with high sensitive cylindrical cavity. The spectra were recorded at room and different temperatures under spectrometer operating conditions given in Table 1. Signal intensities were measured directly from the recorded first derivative spectra, and spectrum area under absorption curves was calculated by double integration technique using Bruker WINEPR program. Sample temperature inside the microwave cavity was monitored with a digital temperature control unit (Bruker ER 411-VT). This unit provided the opportunity of measuring the temperature with an accuracy of ± 0.5 K at the site of the sample.

A set of three different samples irradiated at a dose of 10 kGy was used to determine the kinetic behaviors of the contributing radical species. To achieve this goal, the samples were heated to predetermined temperature and kept at this temperature for about 5 min; then, their ESR spectra were recorded. The signal intensity data were used to calculate the decay characteristics of radical species responsible for the ESR spectra of gamma-irradiated NaEDTA.

3. Results and discussion

Irradiated polycrystals of NaEDTA were observed to present an ESR spectrum consisting of many unresolved strong and weak resonance lines (Fig. 1). Room temperature spectra were calculated to spread over a magnetic field range of 7 mT and centered at about $g=2.00275$. Overlapping of the ESR signals originating from contributing species created difficulties in the determination of the features of each radical directly from experimental spectra.

3.1. Variations in the signal intensities with microwave power

Samples irradiated at a dose of 10 kGy were used to determine the microwave power saturation features of associated radical species. Variations in the assigned line intensities with microwave power were investigated both at room temperature (290 K) and at 130 K in the ranges of 0.0064–12.7 and 0.001–1.0 mW, respectively. At room and low temperatures, the weak lines were screened by the strong line (Fig. 1b) due to saturation above 3.2 and 0.4 mW, respectively. Spectrum overlapping caused some difficulties in the evaluation of the weak lines. Therefore, only saturation results obtained at room temperature for strong line intensity I are given in Fig. 2. The line intensity was observed to exhibit the same saturation behavior at room temperature and 130 K. Observed differences in the saturation behaviors of the strong and weak intensities point out the presence of different kinds of radical species in gamma-irradiated NaEDTA. It is seen

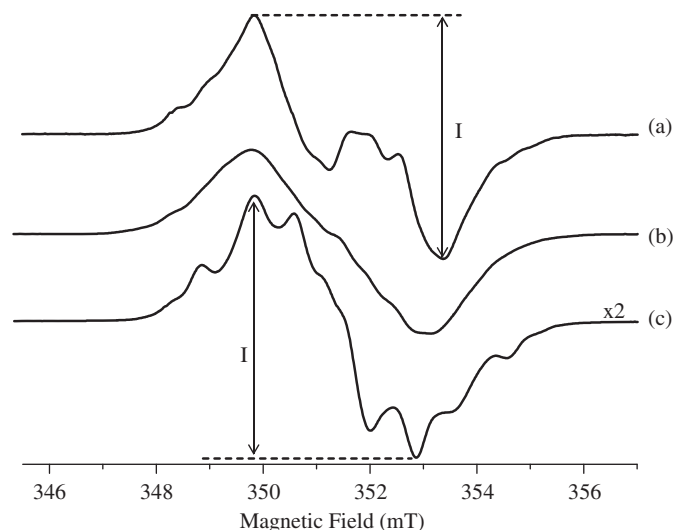


Fig. 1. ESR spectra of NaEDTA irradiated at 10 kGy: (a) room temperature spectrum; (b) the spectrum that was taken at 130 K and 1 mW and (c) the spectrum of the annealed sample at 400 K and cooled down to the room temperature (room and high temperature spectra were taken at 0.64 mW).

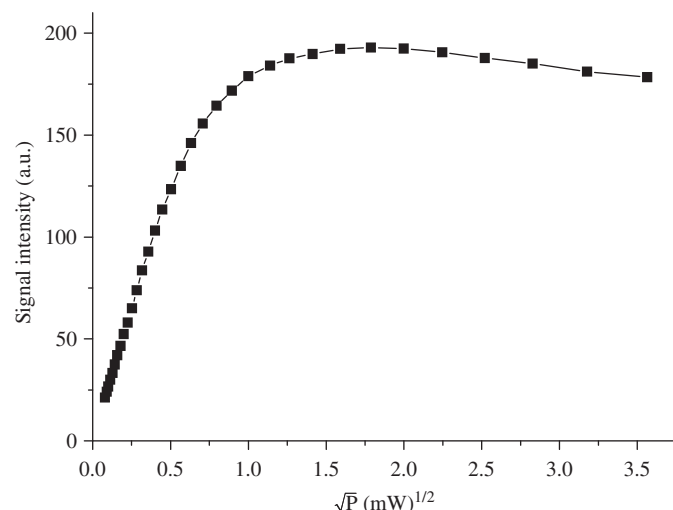


Fig. 2. Microwave power saturation behaviors of the room temperature spectra of the strong line I.

that the strong line that appears as an unresolved doublet due to the radical R1 proposed by Köksal and Osmanoğlu (1993) and has the form of CH_2COOH^- starts to saturate at about 0.8 and 0.04 mW at room temperature and 130 K, respectively. Unfortunately, other lines contributed from radical R2, which has the form of $\dot{\text{C}}\text{H}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{Na})$ were strongly disturbed by the strong line, and it makes difficult to evaluate the variations in these lines versus microwave powers.

3.2. Variable temperature studies

Variations in the monitored intensities with temperature were also investigated using a sample irradiated at a dose of 10 kGy in the temperature range of 130–390 K. Preliminary to the study, care was taken with the level of microwave power to avoid saturation even at the lowest temperature (130 K) achievable in the present work. Thus, the spectrometer operation conditions given for the low temperature condition in Table 1 were adopted throughout the variable temperature studies. The sample was first cooled down to 130 K starting from room temperature

(290 K) with an increment of 20 K. Then the temperature was increased up to 390 K with the same increment and decreased again to room temperature. Below room temperatures reversible changes were observed as expected but above room temperature the signal intensities show irreversible changes and at about 370 K the spectrum changed, as shown in Fig. 1c. Moreover, after cooling the sample to room temperature (290 K), shape of the spectra was not reduced to the original room temperature form (see Fig. 1a). As shown in Fig. 3 the difference between the starting spectrum area and final spectrum area was only 10%. Therefore, the dramatically decrease in the measured signal intensity did not indicate the radical fading.

3.3. Room temperature signal intensity decay in long term

Determining the room temperature radical stability is one of the most important parameters in ESR dosimetry and in discrimination of irradiated samples from unirradiated ones. Sample irradiated at a dose of 10 kGy was stored at room temperature open to air over a storage period of 3 months and its spectra were recorded in regular time intervals. Collected decay data relevant to the interested resonance line *I* are presented in Fig. 4. As it is seen ESR signal intensity experiences fast decays at the beginning

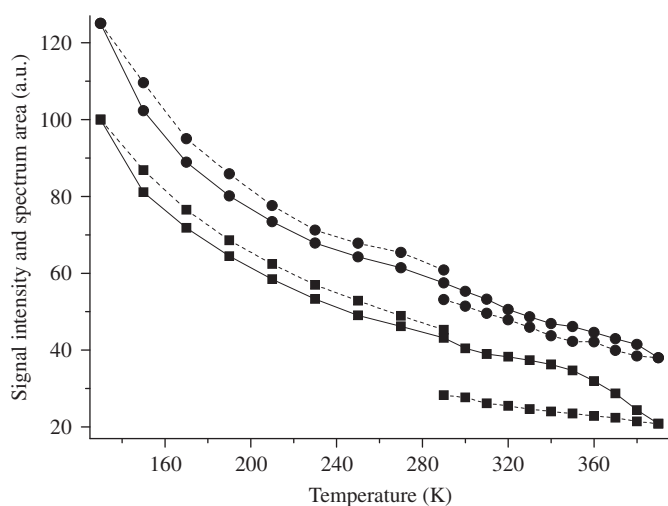


Fig. 3. Variation in the signal intensity of *I* (■) and spectrum area (●) with temperature in the range of 130–390 K; (—) cooling and (---) heating

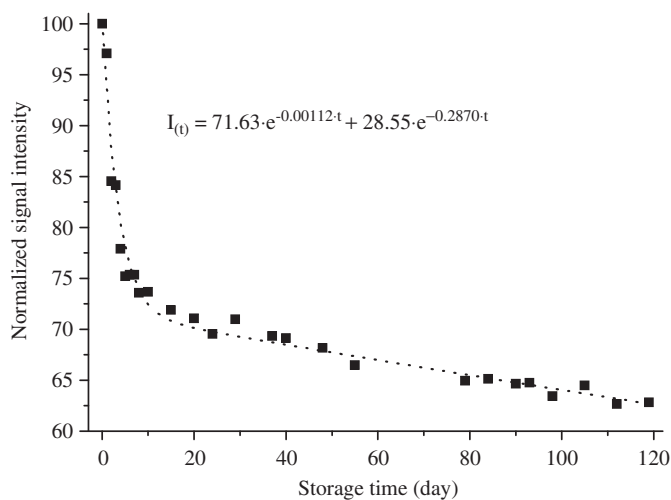


Fig. 4. Variations in the signal intensity with storage time.

of the storage period, and after two weeks more than 25% of the total radical amounts were decayed. After 20 days, it continued to decrease but with much lower decay rates.

In agreement with the results of microwave saturation and variable temperature studies reported in the present work and with the literature findings on irradiated EDTA and DTPA (Köksal and Osmanoglu, 1993), two radical species with different decay characteristics were predicted to take part in the formation of the experimental ESR spectrum of gamma-irradiated NaEDTA. The measured room temperature decay data of the monitored line intensity were fitted to function $I(t) = I_{10}e^{-k_1t} + I_{20}e^{-k_2t}$, which consists of the sum of two exponential decay functions. These functions presenting the characteristics of the first order decay kinetics and *I* and *k* are the percent weights and decay constants of the involved radical species, contributing to the signal intensity of interest, respectively, and *t* is the time elapsed after stopping irradiation.

3.4. Annealing studies at high temperatures

Variations in the line intensities above room temperature (370, 380, 390 and 400 K) were also studied to get information about high temperature decay kinetics of the radicals produced in gamma-irradiated NaEDTA. Intensities were normalized to the intensities measured from the first spectrum recorded 5 min after positioning the sample in the microwave cavity to establish initial thermal equilibrium. Variations in the signal intensity (*I*) at the annealing temperatures are given in Fig. 5 for a sample irradiated at a dose of 10 kGy. As for room temperature decay calculations the high temperature decay constants (*k*) of the radical species were calculated by fitting high temperature signal intensity data to functions comprising exponential terms of different weights and different constants. The decay constants calculated are presented in Table 2. Derived decay constants were used to calculate theoretical variations in the measured quantities. The results related with signal intensities are presented in Fig. 5. It is seen that calculated decay constant describes fairly well the variations in signal intensity at the annealing temperatures. Activation energies of the involved species were also calculated from the Arrhenius plots, and the values presented in Table 2 were obtained.

3.5. Dose–response curves

Dosimetric potential of NaEDTA was explored through the variations in the assigned resonance line intensities and spectrum

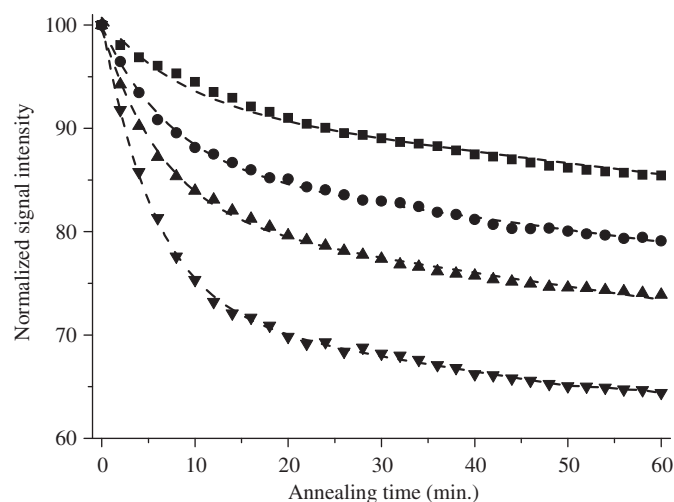


Fig. 5. Variations in the signal intensity with annealing time at four different temperatures: 370 K (■); 380 K (●); 390 K (▲) and 400 K (▼).

Table 2
Decay constants and activation energies calculated for responsible radical species at four different annealing temperatures.

Species	Decay constants ($\times 10^{-3}$) (min^{-1})				Activation energy (kJ/mol K)
	370 K	380 K	390 K	400 K	
R1	1.24	1.45	1.72	2.04	15.70 ± 2.45
R2	119.24	137.52	153.93	176.03	20.46 ± 3.71

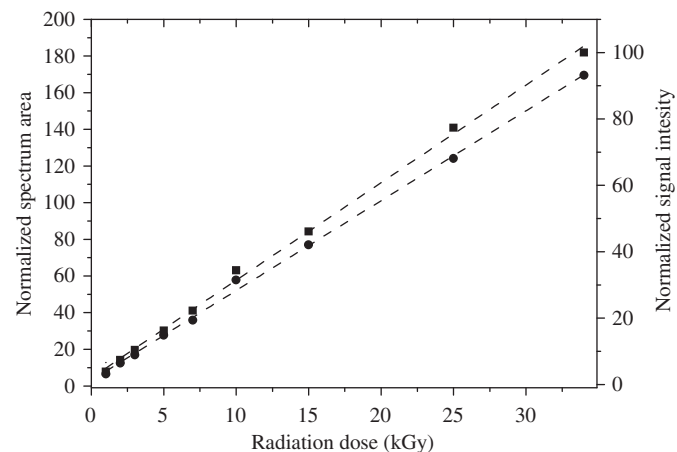


Fig. 6. Variations in the signal intensity and spectrum area with applied dose. I (■); spectrum area (●). Dashed lines: theoretical results obtained by fitting experimental data to a linear function.

area with applied gamma radiation dose. Samples irradiated to doses of 1, 2, 3, 5, 7, 10, 15, 25 and 34 kGy were used to construct experimental dose–response curves. The results are presented in Fig. 6. The choice of appropriate mathematical functions used to describe the dose–response data is important. Linear, quadratic, power, exponential and sum of two exponential have been tried in the present work to describe experimental dose–response data. In these functions (Table 3), I and D stand for the ESR line intensity and absorbed dose in kGy, respectively, and a, b, c, \dots are the constants to be determined. It should be noted that no attempt has been made to force the curves to pass through the origin. There are no significant differences between the correlation coefficients of each function. So the linear function was chosen to construct the dose–response curves.

Although, the signal intensities and the spectrum area of irradiated NaEDTA have a linear dependence on the applied doses, its low radiation yields and its fast radical decay even at room temperature makes NaEDTA a non-ideal dosimetric material. However, it is concluded that ESR spectroscopy could be used in the discrimination of irradiated NaEDTA from the unirradiated one even long after irradiations, and it could be used as a retrospective dosimeter.

3.6. Spectrum simulation calculations

A model based on the presence of two radical species with different spectroscopic features, which are denoted as radical R1 and radical R2, was used to determine the ESR parameters of these radicals by spectrum simulation calculations. ESR signal intensity data derived from the sample irradiated at 10 kGy and heated up to 400 K and cooled back to the room temperature were used to determine the spectroscopic features of the involved radical species. The results of the simulation calculations are presented in Table 4. The radical R1 is an anion radical and the

Table 3
Mathematical functions, parameter values and correlation coefficient best describing experimental dose–response data.

Functions		Spectrum area	I
$I = a + bD$	a	3.103	2.013
	b	4.900	2.940
	r^2	0.9984	0.9980
$I = c + fd + dD^2$	c	1.933	0.490
	f	5.186	3.312
	g	−0.008	−0.011
	r^2	0.9986	0.999
$I = hD^j$	h	6.155	3.839
	j	0.938	0.927
	r^2	0.9987	0.9989
$I = k + (1 - e^{-mD})$	k	862.664	396.106
	m	0.006	0.009
	r^2	0.9984	0.9990
$I = n(1 - e^{-pD}) + q(1 - e^{-sD})$	n	387.023	110.089
	p	0.009	0.007
	q	748.607	274.696
	s	0.003	0.010
	r^2	0.9984	0.9990

Table 4
Spectroscopic parameters calculated for contributing radical species.

Radical species	Percent concentration	Linewidth (mT)	g values	Hyperfine splitting (mT)			
				A_{xx}	A_{yy}	A_{zz}	
R1	87.68	1.24	$g_{\text{iso}} = 2.0037$	H_x	1.21	0.96	1.79
R2	12.32	0.23	$g_{xx} = 2.0061$ $g_{yy} = 2.0015$ $g_{zz} = 2.0014$	H_β	0.95	0.93	0.93

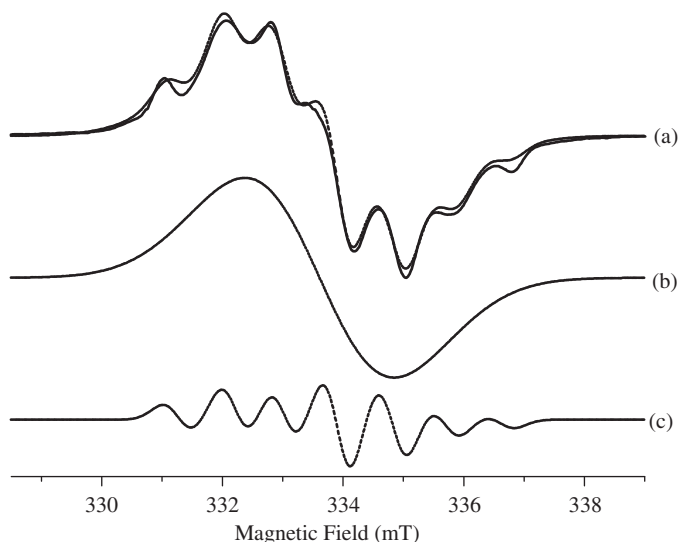


Fig. 7. Experimental (solid line) and theoretical (dashed line) ESR spectra calculated using parameter values given in Table 4. (a) Sum spectra; (b) spectra of radical R1 and (c) spectra of radical R2.

unpaired electron interacts with three equivalent protons but this interaction is screened due to the broad linewidth and its ESR spectra look like a singlet. Radical R2, in which the unpaired electron interacts with the two methylene groups, has the form of $\dot{\text{C}}\text{H}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{Na})$. The spectroscopic parameters

and percent concentration of these two radicals are calculated using a homemade simulation program and are given in Table 4. The theoretical spectrum of each species and their sum were also calculated. They are shown in Fig. 7 together with their experimental counterpart for comparison. As shown in the figure, the agreement between theoretical and experimental spectra is fairly good.

4. Conclusion

Irradiation of NaEDTA with γ -radiation produces free radicals that are detectable by ESR. The ESR spectra of irradiated NaEDTA consisted of many unresolved resonance lines in which the weak lines were screened by a strong line. The investigations in the present work indicate that a model based on the presence of two radical species denoted as R1 and R2 of different spectroscopic and decay features was found to describe well the experimental results derived in the present work. Although at the beginning of storage the decay of the radicals at room temperature was fast the ESR spectrum of irradiated NaEDTA could be detected even after a storage period of 3 months and that ESR spectroscopy could be used for discrimination of irradiated NaEDTA from the unirradiated one.

The decays of the assigned line above room temperature are relatively fast. Above 370 K the spectrum changed and the weak lines were easily distinguished from the spectrum but still overlapped with the strong line. When the sample was cooled down to the room temperature the shape of the spectra did not return to the unheated sample spectra. The spectrum area investigations show that only 10% of the total amounts of the radicals were decayed during heating–cooling treatment. It is concluded that the crystal water of the samples was removed, and it caused a dramatic change in the ESR spectra of irradiated NaEDTA. Although its fast decay characteristic of NaEDTA at the beginning of the storage period at room temperature and high temperature

annealing study (400 K) only about 35% of the signal intensities were decayed at the end of 120 days and 1 h, respectively. It is concluded that ESR signals of irradiated NaEDTA were distinguishable long after the radiation process even at room and high temperatures.

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