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Decomposition study of the electron paramagnetic resonance spectrum of irradiated alanine

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Abstract

Recent Electron Paramagnetic Resonance (EPR) studies on alanine powders as a function of irradiation dose and temperature on the one hand and single crystal Electron Nuclear DOuble Resonance (ENDOR) studies on the other hand, showed the presence of at least three radicals contributing to the total alanine EPR spectrum. The latter spectrum obtained after irradiation at room temperature (RT), is dominated by the well-known stable-alanine-radical (SAR) $CH_3C^{\bullet}HCOO^-$, also denoted R1. Appropriate heating of irradiated alanine causes the relative contribution of R1 to decrease, resulting in a spectrum mainly caused by the H-abstraction radical $CH_3C^{\bullet}(NH_3^+)COO^-$, denoted R2. Although the EPR spectrum of these two radicals could be satisfactorily simulated, their influence on dose reconstruction has not been reported yet. Therefore, a detailed Maximum Likelihood Common Factor Analysis (MLCFA) study has been performed on EPR spectra from polycrystalline alanine samples, after irradiation and heat treatments. Conclusions concerning the number of contributing radicals and their influence on the RT irradiated alanine EPR spectrum will be made. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Alanine; EPR spectrum; MLCFA; Spectrum decomposition

1. Introduction

Alanine has already been studied for many years from both the fundamental and dosimetric point of view. Long before the widespread use of alanine as part of a dosimetric system, irradiated alanine single crystals were found to be interesting materials to be studied by Electron Paramagnetic Resonance (EPR) at both room and low temperature. The structure of the dominant radical present after exposure to ionizing radiation, was extensively studied by several researchers [1–8]. Next to EPR, also Electron Nuclear DOuble Resonance (ENDOR) measurements at low temperature were undertaken in order to determine the

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structure and the environment of the observed paramagnetic defects [9,10]. Since the work of Regulla and Deffner [11] the use of alanine as a multi-purpose dosimeter knew an expansive growth in high-dose dosimetry applications, including food preservation, sterilization of medical supplies, industrial radiation processing and biological research. Other promising applications are situated in the field of radiation therapy where lower doses are appropriate [12]. In many respects it is difficult to think of an alternative dosimeter with the same excellent applicabilities. Inherent advantages of the alanine/EPR dosimetric system, are e.g. its very close equivalency with living tissue, good dose-yield factors, linear signal response over a wide range of radiation doses, reproducible fading characteristics and the non-destructive, fast and straightforward EPR-readout technique. Since a few years, portable EPR spectrometers have been specially designed for the purpose of routine dosimetry, to avoid the purchase of high cost EPR spectrometers which are mainly intended for fundamental research. However, fundamental studies remain indispensable for a reliable use of the dosimeter. Such studies were often concentrated on the behaviour of one or more characteristics of the powder alanine EPR spectrum, directly related to its application (e.g. central EPR line, spin-flip lines). The influence of the dose, dose rate, radiation quality (e.g. X-, α-, β-, γ-, p-, n-rays) and environmental parameters (e.g. humidity, storage temperature, light exposure), etc was studied.

Other research groups were more concerned with the composite character of the alanine spectrum. It is well-known, e.g. from the field of EPR dating, that disregarding the compositeness of a spectrum, dose assessments, using either peak-to-peak methods or other methods assuming the presence of only a single paramagnetic defect, can yield erroneous dose estimations [13]. On several occasions, indications of the composite character of the alanine spectrum were found. In the last few years however, an increasing number of papers have proven the alanine spectrum to be at least threefold composite. Examining the effect of UV light exposure on irradiated alanine detectors, Wieser et al. [14] found that each of the five lines of the usual alanine spectrum seemed to split into a doublet possibly due to a secondary radical species. Callens et al. [15] demonstrated by using a multi-variate statistical decomposition method, Maximum Likelihood Common Factor Analysis (MLCFA) (De Volder et al. [16]), that the EPR spectrum of alanine is a composite of at least three components over the dose range of $1–10^6$ Gy. Rakvin [17] has shown by using Double Modulation EPR (DMEPR) that the DMEPR spectra of alanine could be better simulated by assuming the existence of two radical species with different spin-lattice relaxation times (T_1) for room temperature (RT) irradiated alanine. Nagy et al. [18] observed variations in the EPR signal intensity of L-α-alanine within hours and days after γ-irradiation. The character of the time dependence of the amplitude varies with dose and the amplitude changes reach 1–1.5%. It was concluded that the observations favour the hypothesis that irradiated alanine contains several paramagnetic centers. Recently Sagstuen et al. [19] undertook a detailed EPR, ENDOR and ENDOR Induced EPR study of radical formation in single crystals of L-alanine at RT. It was found that at least two other radicals are present together with the well-known R1 alanine radical and that one of these (R2) is present in a relative amount comparable to that of R1. They assigned the R2 radical to a species exhibiting the structure H_3N^+-$C^\bullet(CH_3)C(=O)O^-$. The third species R3 was tentatively assigned to a radical with the structure H_2N-$C^\bullet(CH_3)C(=O)O^-$. In a previous paper (Vanhaelewyn et al. [20]), the effect of heating on the EPR spectrum of polycrystalline alanine recorded at RT was studied. Samples of L-alanine were irradiated with X rays at both RT and temperatures up to 250°C. It was found that upon heating RT irradiated alanine powder, a strong decay of the signal was observed. Moreover, features of the spectrum ascribed to the R2 radical become more pronounced, providing an experimental isolation of this second alanine radical. The same spectrum of R2 could be retrieved by the high temperature irradiations. By the use of MLCFA it was determined that three components in irradiated alanine powder behave differently as a function of temperature. The spectra of

two of these components (R1 and R2) could be isolated using simulations with the most recent spin-Hamiltonian parameters. In order to find out whether the three components found by Callens et al. [15] by applying MLCFA on a dose series of alanine spectra and those found in the previous paper with MLCFA on temperature series of alanine spectra, are the same, a more extensive MLCFA study was undertaken. A larger number of samples irradiated at different doses and corresponding heated samples have been compared.

2. Experimental

2.1. Material and irradiations

For all experiments, L-α-alanine powder (Aldrich) with grain size in the range of 100–200 μm was used, in the absence of any binder material. The X-irradiations were carried out at the 15 MeV linear electron accelerator facility of the University of Ghent [21]. The X-ray beam was produced with a 800 μA 10 MeV electron beam hitting a tantalum/graphite bremsstrahlung target designed to withstand the high electron beam power density involved [22]. The endpoint energy of the bremsstrahlung beam was 10 MeV and the mean photon energy was 1.8 MeV. Absolute dose calibration was performed with a chemical dosemeter using a ferrous Fricke solution. All irradiations were performed in air at RT in the dose range 1 Gy–1 MGy. In this way 31 samples were obtained (1, 2, 4, 6, 8, 10, 20,…, 8×10^5, 10^6 Gy).

2.2. Instrumentation and methods

All EPR spectra were recorded using a Varian E-line X-band spectrometer with a maximum microwave power of 200 mW. The magnetic field was modulated at 10 kHz with a peak-to-peak amplitude of 0.1 mT. The spectra were recorded in a single scan with a sweeptime of 600 s and a time constant of 1 s in the magnetic field range 330.0–348.0 mT. A microwave power of 1.0 mW was applied for all spectra. Four temperature series of spectra were realized, each starting from an alanine sample irradiated with a specific dose (1 k, 10 k, 100 kGy and 1 MGy) and by subsequently heating the sample at a constant temperature (approximately 260°C) for times varying between 10 and 100 s. Only spectra recorded at RT were included in the analysis. The samples were heated using an ELF 10/14 Carbolite-Furnaces oven allowing a maximum heating temperature of 1000°C. The temperature at the position of the sample was measured with a 9001 thermometer from Comark. For all EPR measurements (50.0 ± 0.1) mg of irradiated alanine was used. The alanine samples for the dose series were put into 5 mm O.D. Wilmad quartz tubes while the samples used for the heating sequences were put in longer tubes allowing easy transfer from the oven to the cavity without any loss of sample. All EPR spectra have been normalized to a microwave frequency of 9.50 GHz. The magnetic field and the microwave frequency were measured using a Bruker B-NM12 NMR gaussmeter and a HP 5342 A microwave frequency counter, respectively. For absolute g-value determinations, a calibration using the g-standard DPPH ($g = 2.0036$) was performed.

2.3. MLCFA

In order to determine the number of EPR components contributing to a set of experimental spectra, a multi-variate statistical decomposition method, called MLCFA was used. The method was recently introduced for the analysis of composite EPR spectra [15,23,24]. The underlying principle of MLCFA is the assumption that each observed spectrum is linearly influenced by a small number of hypothetical constructs (e.g. the contribution of a specific radical), called common factors. A factor is called common if it contributes to at least two observed spectra. MLCFA assumes that the correlation between the observed spectra is solely due to a small number of common factors. Best results are obtained when the observed spectra are influenced by as many experimental parameters as possible. The experimental parameters used in this study are the irradiation dose and a combination of heating time and temperature. All spectra should preferably be

recorded strictly under identical conditions to avoid artefacts.

The values of the different parameters in the MLCFA model are estimated by the minimization of the so-called likelihood function. In order to determine the correct number of common factors, a sequential procedure with a stepwise increasing number of common factors is used. The common factors are predicted using a linear regression method. The common factors obtained in this way are called abstract because they usually are a linear combination of real component spectra. A real component is defined as a physically relevant EPR component, that contributes to an experimental spectrum. The spectrum of a real component can in principle be isolated using either experimental or numerical methods. Different related sets of spectra containing the same real component spectra, when analysed by MLCFA, may result into different but mutually linearly dependent sets of abstract common factors. Finally, these abstract common factors need to be transformed into an equal number of real component spectra. This can be accomplished by a minimization procedure which tries to fit a simulated spectrum (governed by a set of spin Hamiltonian and line shape parameters) to a linear combination of common factor spectra. This last step is far from obvious in the case of irradiated alanine, since accurate powder simulations are required for all the contributing components. Moreover, a real component can be a composite of two or more different single components each originating from a single type of radical. This is the case when two or more single components behave in the same way e.g. as a function of applied dose, temperature or another possible influencing parameter implying that the sum of the spectra of these components does not change its shape.

The essential elements of the MLCFA procedure are the number of common factors, the percentage variance, the percentage cumulative variance, the abstract common factors themselves and the real common factors. The percentage variance of a common factor is the percentage of the total variance for which this factor accounts. For a mathematical description, we refer to De Volder et al. [16]. The percentage cumulative variance is the sum of the percentage variances for all factors. From previous MLCFA studies, it is very important to note that:

1. The variance of an abstract factor does not reflect the relative importance of a real component contributing to a set of spectra. The first abstract common factor will usually account for a high percentage of the cumulative variance. However, this does not necessarily mean that the additional real components are of minor importance. Nevertheless, an unimportant real component has also little effect on the cumulative variance upon considering it (via the addition of an extra abstract factor).
2. The number of common factors are lower limits for the total number of single component spectra. Since two single components behaving the same way (e.g. as a function of dose, temperature, etc.) will not be distinguishable by MLCFA, their weighed sum will result into one single real component.

In practice essentially the following procedure was followed: a particular set of experimental spectra was tested for an increasing number of abstract common factors. We stopped the routine when the root mean square (r.m.s.) deviation between the experimental spectra and the corresponding linear combinations of the abstract common factors did not exceed a certain value. The latter is equivalent but more objective than requiring that all experimental spectra are de visu fairly well reproduced by linear combinations of these common factors. The second parameter which accounts for the quality of the spectral reproduction and that was considered in the routine, was the percentage cumulative variance. The routine was also stopped when the percentage cumulative variance did not increase by more than a certain threshold, when the number of common factors was increased by one. The latter threshold may depend on many experimental factors (e.g. choice and number of spectra to be analysed, quality of magnetic field and microwave frequency calibration, noise level of the spectra, etc).

To simulate the single component EPR spectra of the alanine radicals, we used a program developed at the Linköping University [25]. This program takes the contributions of the forbidden

transitions as a function of microwave power into account. Simulations were performed on a Sun UltraSPARC workstation. To estimate the relative contributions of the real components to the total spectrum, the double integral of the individual components was normalized to an intensity of one. For more detailed information about the application of MLCFA to the decomposition of multicomponent EPR powder spectra, see Moens et al. [23]. The MLCFA software was purchased from FACTORSOFT, Belgium.

3. Results

Recently it has been undoubtedly proved that irradiated L-alanine has a composite EPR spectrum. Investigations with MLCFA on dose series (Callens et al. [15]) and on temperature series of alanine spectra using a high temperature cavity (Vanhaelewyn et al. [20]), revealed the existence of at least three different real components contributing to the alanine spectrum. The compositeness of the spectrum is however not clearly discernible by visual inspection of the RT irradiated alanine spectra. The only visible changes that occur in the shape of the alanine spectrum are mainly an apparent or real broadening of the lines at high doses, accompanied by a loss of structure in the spectrum. As an illustration, two spectra, from a 10 kGy and 400 kGy sample, respectively, have been scaled to the same signal height and displayed in Fig. 1. On the other hand, the compositeness of the alanine spectrum is clearly observed after heating an irradiated alanine sample at a suitable temperature for a certain time. Significant changes become then visible in the spectrum which are mainly due to the decay of the R1 component. Applying an appropriate heat treatment (around 250°C), the spectrum of R2 can be isolated (Vanhaelewyn et al. [20]). As an illustration of the result of such a treatment, the retrieved spectrum of R2 has been displayed in Fig. 2, together with the spectrum of an unprocessed sample. Note that both spectra have been recorded at RT and that the spectrum of R2 has been scaled to its contribution as calculated from the unprocessed spectrum.

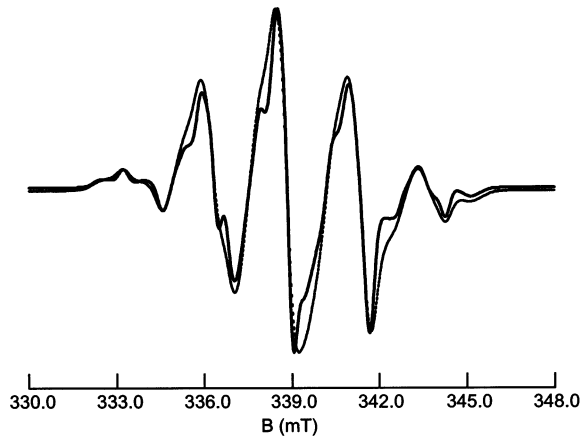

Fig. 1. Illustration of the effect of dose on the shape of the alanine EPR spectrum. The spectra in solid and dashed lines are from samples X irradiated with 10 kGy and 400 kGy, respectively. The two spectra have been scaled to the same signal height for comparison. When carefully inspecting the two spectra, it is seen that the width of the central line from the 400 kGy sample is broader than that of the 10 kGy sample. This line width has been plotted as a function of applied dose in Fig. 4.

3.1. MLCFA analysis of the dose series

For the first MLCFA analysis, the original dose series was divided into four partially overlapping subseries. The first, second, third and fourth sub-

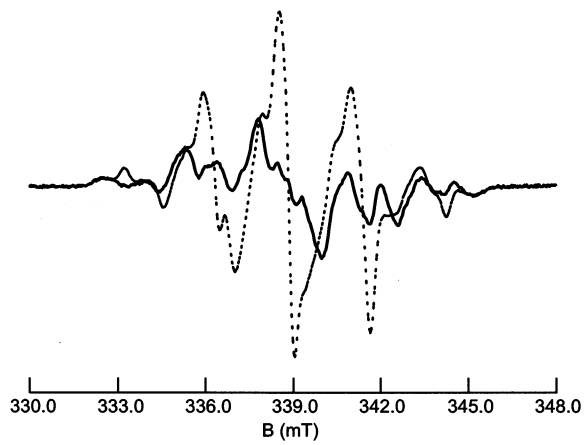

Fig. 2. Comparison of the isolated ten-line spectrum (solid line) originating from the R2 radical with the initial spectrum of an X irradiated L-alanine sample (dashed line). The ten-line spectrum was isolated by carefully processing the sample using a high temperature cavity (Vanhaelewyn et al. [20]).

Table 1
Variance analyses of the common factor solutions for the 10 Gy–1 kGy, 100 Gy–10 kGy, 1 kG–100 kGy and 10 kGy–1 MGy dose range

Dose range	Number of common factors	Variance (%)	Cumulative variance (%)
10 Gy–1 kGy	1	93.833	93.833
100 Gy–10 kGy	1	99.887	99.887
1 kGy–100 kGy	1	98.915	98.915
	2	1.062	99.977
10 kGy–1 MGy	1	99.242	99.242
	2	0.704	99.946

series consist of samples irradiated with doses ranging from 10 Gy to 1 kGy, 100 Gy to 10 kGy, 1 kGy to 100 kGy and 10 kGy to 1 MGy, respectively. MLCFA was then performed on the spectra for each of the four dose ranges and detected in the first, second, third and fourth subseries one, one, two and two abstract common factors, respectively. The percentage variance and cumulative variance of the four series for increasing numbers of common factors are displayed in Table 1. At first sight this would let us conclude that two real components are involved in subseries three and four and that only one real component is present in the first and second subseries. In Fig. 3a and b, the abstract common factors found in the dose range 1 kGy–100 kGy have been displayed. The common factors found in the dose range 10 kGy–1 MGy are very similar. Considering the presence of at least the two components R1 and R2 from previous work [19,20], it was however not possible to isolate any of these components separately. A third component (e.g. R3) might however be the reason for the second common factor, assuming that R1 and R2 account for only one real component (i.e. they have exactly the same dose response). On the other hand, plotting the width of the central line in the alanine spectrum against the applied dose results in Fig. 4. It can be seen from this figure that below 10 kGy the width of the central line remains more or less constant but increases dramatically from about 0.53 mT at 10 kGy to about 0.78 mT at 400 kGy and then decreases again. These findings led us to investigate the influence of line broadening on the number and character of abstract common factors in alanine spectra. To examine this effect, a simulated set of spectra was constructed from only the major components R1 and R2 with comparable contributions and varying line widths increasing with dose as in the experimental spectra. MLCFA computed very similar common factors as in the experimental case (compare Fig. 3c and b). Note that all simulated spectra in the set are unique in such a way that none of these spectra can be written as a linear combination of any number of other spectra from the set. From the physical point of view we would expect the number of common factors to be zero, since no factors are common in the simulated set of spectra. As outlined in the basic principles of MLCFA, the statistical decomposition method assumes a small number of common factors to be on the basis of any spectral changes in the set of spectra. Thereby MLCFA does not consider nonlinear spectral changes caused by e.g. line broadening. The consequences on the number and nature of common factors is somewhat unpredictable. Therefore, the second common factor in the third and fourth subseries are abstract common factors artificially constructed in a way that they compensate as well as possible for the effect of line broadening in the experimental spectra. Extending the third subseries towards larger doses results into a larger number (i.e. three) of common factors required to compensate for changes in the line width.

3.2. MLCFA analysis of the temperature series

As outlined in the Instrumentation and methods, four heating series were constructed, starting from a 1 kGy, 10 kGy, 100 kGy and 1 MGy irradiated alanine sample, respectively. MLCFA revealed three abstract common factors in the 1 kGy and 10 kGy heating series (in agreement with [20]) and four abstract common factors in the 100 kGy and 1 MGy heating series. The statistical results for the four series are shown in Table 2 and, as an example, the common factors of the 10 kGy temperature series have been displayed in Fig. 5. Using the common factors of each of the heating series, it was possible to adequately reconstruct R1 and R2. An illustration of this isolation is shown in Fig. 6 where the simulations of R1 and R2 are plotted as well as the best linear fit of the abstract common factors from the 10 kGy heating series. To compute the simulations, the most recent spin-Hamiltonian parameters from literature were used (Sagstuen et al. [19]). Only one minor approximation was necessary i.e. the g-tensor of R2 was taken to be isotropic with a g-value of 2.0025 since no complete g-tensor has been reported yet for this component. The fact that both R1 and R2 components could be isolated from the common factors, means that both components are in fact single real components that behave differently as a function of absorbed heat. We expect also a third radical species (R3) to contribute to the common factors if this component also varies differently from R1 and R2. Indications show that a third radical species disappears after a few heating cycles, suggesting that this species is less stable than R1 and R2. The latter could be proved by subsequently removing the first spectra from the heating series. At a certain point, the number of common factors decreased to two for all series. For the 1 kGy and 10 kGy series this means that the third radical, probably R3, is very unstable at 260°C. Unfortunately, appropriate spin-Hamiltonian parameters have not yet been reported to allow adequate

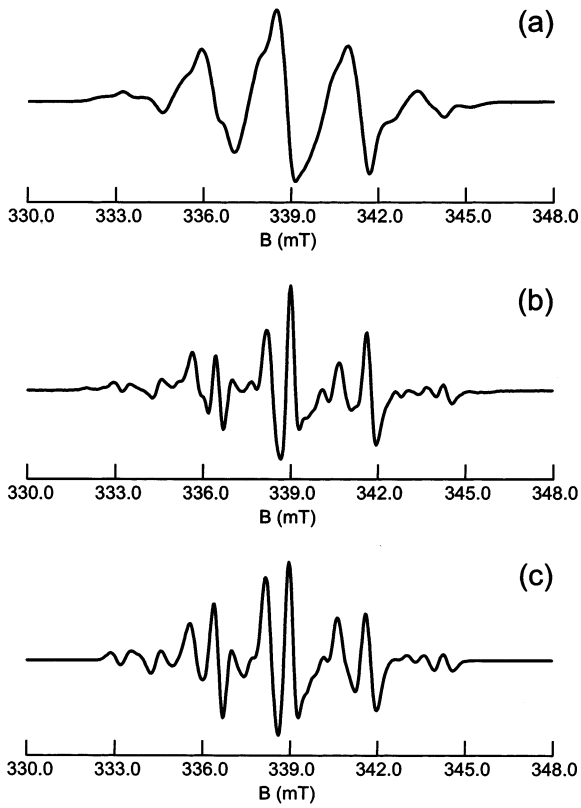

Fig. 3. The two abstract common factors (a) and (b) from the L-alanine spectra in the dose range 1 kGy–100 kGy. The first common factor (a) resembles strongly an experimental spectrum and the second common factor (b) is caused by line broadening occurring in this dose range. Spectrum (c) is the second abstract common factor from a simulated set of spectra with comparable line width and intensity as the experimental set for the 1 kGy–100 kGy dose range.

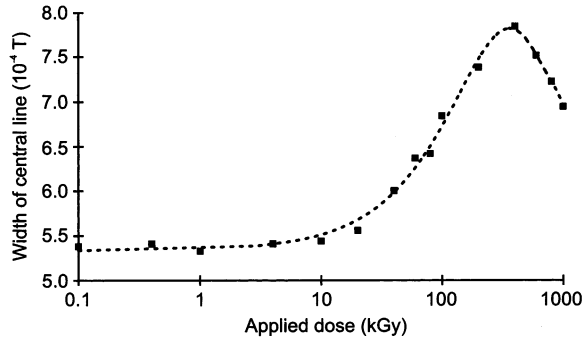

Fig. 4. Apparent width of the central line in the L-alanine spectrum against the applied dose. Below about 10 kGy, the line width remains constant (≈ 0.53 mT), while above 10 kGy, the line width increases up to a maximum (≈ 0.78 mT) at about 400 kGy and then decreases again.

simulation of this third real component and it could thus not be reconstructed from the abstract common factors.

For the 100 kGy and 1 MGy series however, four abstract common factors were found. The third real component is probably also related to R3 whereas the fourth component accounts for line width effects. The line width effect was not surprising for the 100 kGy and 1 MGy samples, since one might assume that the line width will change if the components decay.

Another interesting finding was the fact that, the higher the absorbed dose of the sample, the faster the spectrum decayed as a function of the absorbed heat. This is illustrated in Fig. 7 by the decay curves of R1 and R2 for the 1 kGy, 10 kGy and 100 kGy sample. The contributions of R1 and R2 have been computed by fitting only these two components to the experimental spectra. This implies that R1 and R2 are by far the dominant components, which appears to be a good approximation in view of the quality of the spectrum reproductions. The contribution of R2 to the initial samples was found to be about 40% in the 1 kGy and 10 kGy series. It is also worth noticing that the contribution of R2 in the 1 kGy series stays more or less constant with absorbed heat.

4. Discussion

In a previous MLCFA study performed by Callens et al. [15] on dose series of L-alanine, the number of common factors amounted up to three in all considered dose ranges. In view of the above, the increased number of common factors as compared with our analyses might (partly) be caused by line width effects. To check this hypothesis, analogous sets of spectra were constructed from our more complete set, in order to replicate some of the previous analyses. The results of these tests indeed pointed towards a larger number of common factors upon extending the dose range and considering a smaller number of spectra.

One should thus be careful in drawing conclusions from an MLCFA analysis about the behaviour of R1, R2, R3 and other possible radicals present in irradiated alanine in the dose range above 10 kGy. The second abstract common factor from the two experimental dose series (e.g. Fig. 3b) resembles very much the second common factor from the simulated set of spectra (Fig. 3c). However, when varying the contribution ratios of R1 and R2 in the simulated set of spectra (thus creating a different dose response for R1 and R2 in addition to line width effects), we found also a

Table 2
Variance analyses of the common factor solutions for the 1 kGy, 10 kGy, 100 kGy and 1 MGy samples, repeatedly submitted to a constant temperature (260°C) for 100 s and denoted in the table as temperature series 1, 2, 3 and 4, respectively

Temperature series	Number of common factors	Variance (%)	Cumulative variance (%)
1	1	61.508	61.508
	2	38.194	99.702
	3	0.191	99.894
2	1	68.191	68.191
	2	31.706	99.896
	3	0.064	99.961
3	1	67.349	67.349
	2	32.097	99.446
	3	0.373	99.819
	4	0.029	99.849
4	1	80.700	80.700
	2	16.926	97.626
	3	0.733	98.359
	4	0.208	98.568

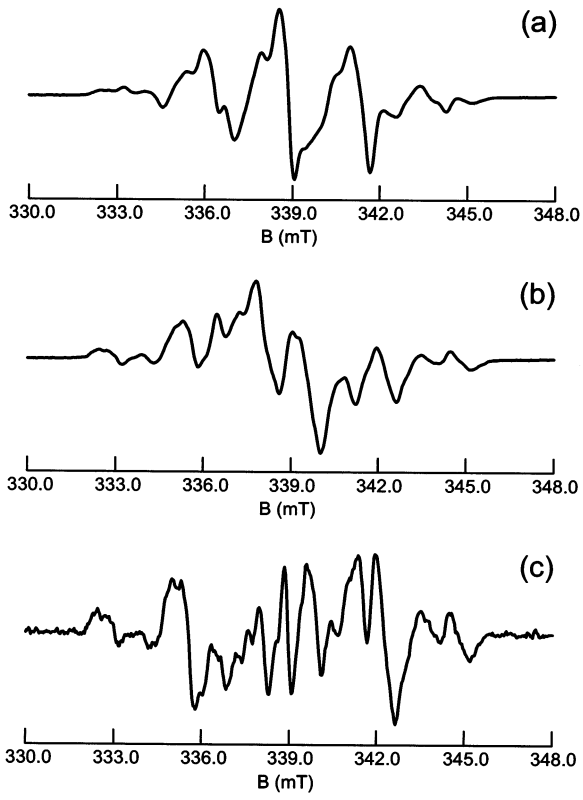

Fig. 5. Illustration of the first (a), second (b) and third (c) abstract common factor spectrum of the 10 kGy temperature series.

second common factor very similar to the one found earlier (Fig. 3c). In fact, from the MLCFA analysis in this dose range, one cannot derive any conclusion about the behaviour of R1 and R2. In general, when the spectrum shape of one or more single components changes as a function of dose or another experimental parameter, the number of common factors becomes practically unpredictable.

The hypothesis that anisotropy in the spectra caused by the finite grain size (100–200 μm) of the alanine samples could have any influence on the number and character of the abstract common factors, was also examined. Several spectra of the same sample were recorded under identical conditions with the only difference that the sample had been shaken between two recordings to produce another arbitrary orientation of the L-alanine crystals. The MLCFA results predicted only one common factor in this set of spectra. Assuming the existence of two components (where the second one should be artificial), the percentage cumulative variance increased only by 0.012%. Moreover, the second common factor could not be related in any way to the additional common factors produced by line broadening. This result excludes also the hypothesis that the effect of anisotropy in the spectra caused by the grain size could be confounded by the effect of line broadening.

So far, we can only conclude that R1 and R2 have the same dose response in the range 10 Gy–10 kGy and that above 10 kGy the relative dose response for the latter components is not known because of the line width effect.

From the quality of the reproduced spectra of the temperature series with only R1 and R2, it is

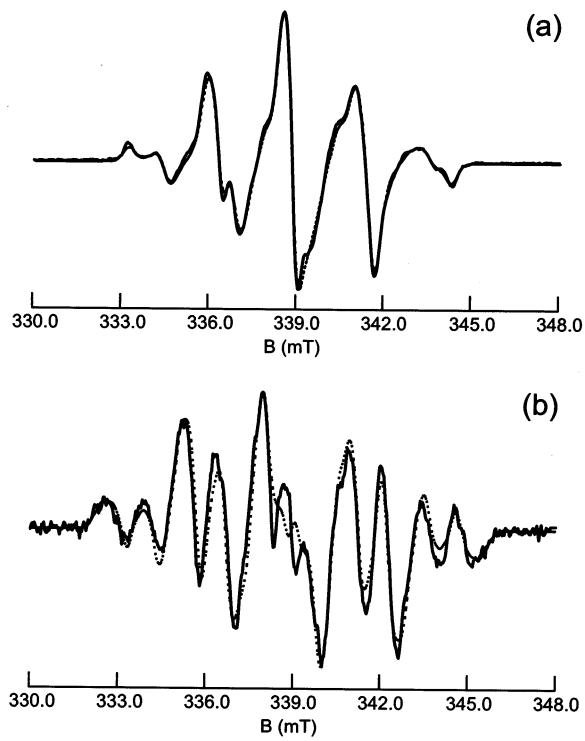

Fig. 6. Isolation of the radical components R1 and R2. The solid line spectra are the best linear fits of the abstract common factors of the 10 kGy temperature series (Fig. 5) to the simulated spectra of R1 (a) and R2 (b) (dashed line), respectively.

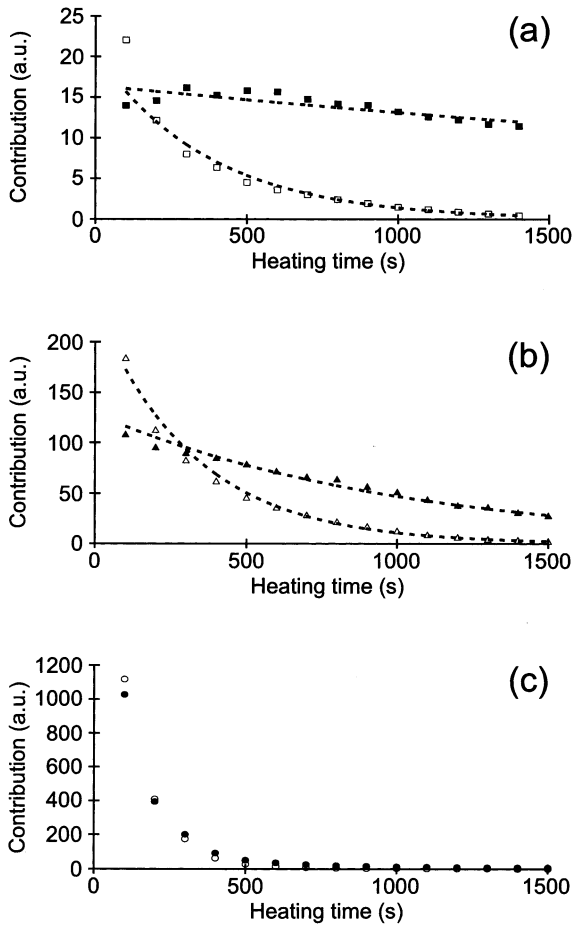

Fig. 7. Decay curves as a function of subsequent heating for the 1 kGy (a), 10 kGy (b) and 100 kGy (c) temperature series. In all three graphs, the filled and open symbols represent the contributions of R1 and R2, respectively. The dashed curves in (a) and (b) are single exponential fits to the experimental data points. In (c) a single exponential fit was not possible.

concluded that the contribution of R3 is not very important compared with the ones of R1 and R2 although considering R3 might improve the spectrum reproduction.

Although the interpretation of kinetic data like the decay curves of R1 and R2 is no trivial task, they are quite informative about the presence of interactions between the radicals involved (R1–R1 and R1–R2). In the case of the 1 kGy and 10 kGy samples, single exponential curves could be satisfactorily fitted to the experimental data (Fig. 7a and b). This probably indicates that each individual R1 and R2 radical decays thermally without intervention of other radicals. This is in agreement with the large distance between the radicals, reflected in a constant line width (Fig. 4). The decay curves of R1 and R2, starting from a 100 kGy or 1 MGy sample, can however not be explained in terms of independently decaying entities. Next to first order decay processes, higher order terms are needed to explain the decay kinetics, implying reactions/interactions between radicals. The vicinity of radicals at higher doses may induce spin-spin interactions, affecting the EPR line width of both R1 and R2.

5. Conclusions

The components R1, R2, R3 and all other possible contributing radicals in the spectrum of X irradiated alanine, have the same response as a function of applied dose up to about 10 kGy. From the dosimetric point of view, this means that the composite character of the alanine spectrum does not have influence on the dose assessment for doses below 10 kGy. Considering the dose range above 10 kGy, no conclusions about the relative dose response of R1 and R2 could be made because it has been shown that applying a decomposition method like MLCFA on spectra with nonlinear spectral changes, e.g. as a consequence of line broadening, is not reliable.

A third minor radical species, probably R3, decays much faster with absorbed heat than R1 and R2. The decay of the dominant components R1 and R2 in high dose samples is indicative of interactions between radicals, compatible with line width effects observed in the alanine EPR spectra. Since high radiation doses might induce less stable, interacting radicals, significant fading could occur in alanine samples irradiated with high doses when stored at temperatures above than RT.

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