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Advancements in accuracy of the alanine EPR dosimetry system
Part III: Usefulness of an adjacent reference sample

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Abstract

High stability of the radiation-induced radicals in alanine and the high reproducibility of alanine response to radiation make it possible to determine radiation doses accurately with Electron Paramagnetic Resonance (EPR) spectral analysis. Small uncontrollable variations of the EPR spectrometer sensitivity, however, can significantly deteriorate the accuracy of the method. The errors due to these variations can be eliminated or markedly decreased if an adjacent reference sample (such as a synthetic ruby crystal) is permanently present in the cavity, and if ratios of the alanine and ruby signal amplitudes are used throughout the dosimetric session instead of the absolute alanine amplitudes. This paper addresses methodological aspects of using such adjacent reference samples in alanine dosimetry and provides illustrations of the usefulness of this technique.

Keywords: Alenine dosimetry; EPR; ESR; Adjacent reference sample; Accuracy; Ruby

1. Introduction

The highly reproducible radiation response of alanine measured by Electron Paramagnetic Resonance (EPR) enables one to evaluate doses with very high accuracy. For example, the overall uncertainty in the measurement of industrial-range gamma-ray doses determined with this method at NIST, is currently specified at only $\pm 1.2\%$ (2σ). Approximately half of this uncertainty can be attributed to the EPR spectrometry. Consequently, the technique demands very high stability in the sensitivity of the EPR spectrometer. In this particular case, the term *sensitivity* is defined as the signal intensity per absorbing paramagnetic center in a sample with a specific composition and shape measured in a specific position and orientation in a specific resonant cavity. For accurate dose assessments, the same sample positioned in a standard way in the cavity must produce the same signal value accurate to at least 1%, regardless of the time and day of the measurements.

This extreme stability is seldom required for most EPR spectroscopy applications, and this level of stab-

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ility is seldom achieved in practice. The sensitivity of EPR spectrometers may vary with time due to a number of factors, some of which are difficult to control. Among them are fluctuations of the power supply voltages, drifts in the characteristics of the spectrometer components due to warming or natural aging, variations in the cavity Q-factor, as well as other less-defined environmental factors. In addition, some of the variations (Q-factor changes) are not caused by changes in the spectrometer response, but by changes in the properties of the sample such as moisture content. Therefore, special means are necessary for monitoring the spectrometer sensitivity in order to make accurate corrections for its fluctuations.

An effective technique to solve the problem is to use the signal of a fixed adjacent reference sample that is permanently present in the cavity in a position different from that of test samples. Its perfectly stable EPR signal should not overlap with the signals of the test samples in order to enable a user to record it with a test sample still present in the cavity, and the amount of paramagnetic centers in it does not need to be known. This technique was first used long ago by Anderson and Weil (1959), and by Singer (1959). In the later era of semiconductor-based EPR spectrometers, which are much more stable than their vacuum-tube-based ancestors, the technique was not frequently used even in quantitative studies. However, it is necessary to revive this technique to address the unusually high precision requirements of alanine dosimetry.

The principle of using an adjacent reference sample is well known. One records its signal before or after recording the signal of the test sample with the same or very similar parameters and with the test sample still present in the cavity. The line(s) of the reference signal may be within the same scan range as the signal of the test sample, but not necessarily so. The intensity of the test sample signal (either the amplitude or the double integral) is then divided by the amplitude of the reference sample line and this ratio is used instead of the absolute value of the test sample signal.

The effect of this technique is two-fold. First, because the reference signal is recorded along with the signal of the test sample, the probability of a significant change in the spectrometer sensitivity in this short period of time is very low. Therefore, the ratio of the two signals is almost independent of the spectrometer sensitivity and the signal is thus converted into a universal scale that is suitable for intersession comparisons. In this way, effects of power voltage variations, slow long-term thermal trends, and similar incidental factors are effectively cancelled out. It should be emphasized that variations of the spectrometer sensitivity due to the above-mentioned factors can be significant. Variations within 1% are common; for some, especially older instruments, they can be several times larger. As a rare example of an unusually unfavorable case, Fig. 1 shows variations of the EPR signal amplitude of a reference sample recorded by a 10-year-old Bruker ESP300E [1] spectrometer over a three-month period. The sample remained undisturbed in the cavity throughout the observation period; there were considerable periods when the spectra were recorded daily at 1.5 h intervals. Fig. 1 shows that the signal variations reached several percent in relatively short periods of time. Of course, such instability is unacceptable for accurate alanine dosimetry.

Second, the adjacent reference sample method is a good means of eliminating variations in signal intensity due to a varying cavity Q-factor. Provided that excessive microwave power is not used, the EPR signal intensity is proportional to the Q-factor. Therefore, the ratio of the signals is virtually independent of the Q-factor. The main source of Q-factor variations in alanine dosimetry is the different and/or changing water content of dosimeters (Sleptchonok et al., 2000). An adjacent standard makes it possible to compare signals of dosimeters with different moisture contents directly; signal changes due to dosimeters with a changing water content are also corrected for by the standard. Without this correction, errors in dose measurements due to the differences in the water content of dosimeters can easily range from one to several percent. On one occasion, a commercial dosimeter containing a

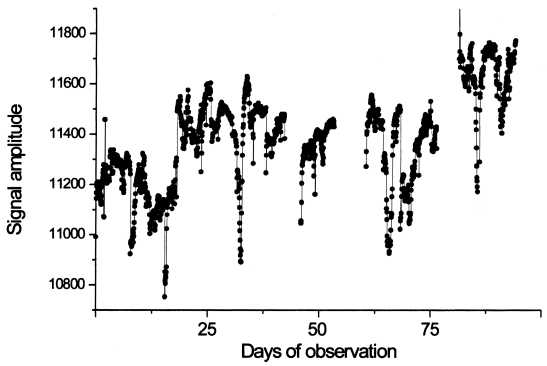

Fig. 1. Variations with time of the EPR signal of a stable paramagnetic material permanently present in the cavity of an older Bruker ESP300 spectrometer. Signal-to-noise ratio was greater than 10,000:1. Microwave power: 0.25 mW, modulation amplitude: 0.5 mT.

[1] The mention of commercial products throughout this paper does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that products identified are necessarily the avilable for this purpose.

metal particle was detected by means of the adjacent standard technique. The particle dramatically decreased the Q-factor and consequently the alanine EPR signal; in the absence of the adjacent reference sample, the calculated dose would be underestimated by several tens of percent.

In principle, many paramagnetic materials can be used as adjacent reference samples. Still, there are some important requirements. Obviously, the signal of a reference sample should be absolutely stable and should not overlap with the signal of the test samples. Its signal should be sufficiently strong to allow acquisitions with good signal-to-noise ratios even when scanning rapidly with a short time constant. The signal of an adjacent reference sample should respond to possible small variations in microwave power and modulation amplitude in the same way as the signal of the test samples. The most reliable solution is to work within the linear ranges of the corresponding dependencies of both samples. It must be possible to record the reference signal with the same or very similar parameters as the signal of the test samples. At the very least, the modulation amplitude should not be changed between recordings in order to avoid instabilities arising from thermal expansion and contraction of the cavity.

Ruby, initially proposed by Singer (1959); Thompson and Waugh (1965), is an ideal material for an adjacent reference sample. Bruker Instruments EPR Division has manufactured a prototype accessory using such a standard. Two views of the prototype that has been tested at the alanine dosimetry facility at NIST are shown in Fig. 2. A small (about 5 mm long, 0.4 mm in diameter) synthetic ruby crystal containing about 10^{-2}% chromium (3+) is mounted on a plunger controlled by a precise micrometer mechanism. The device can be attached to the front wall of a Bruker ER 4103TM cavity so that the ruby crystal can be introduced reproducibly into the cavity through the slots for illumination. This design facilitates the crystal motion independently along its axis and its rotation about that axis. Rotation of the crystal makes it possible to get convenient line positions and adjustment of the depth of the crystal insertion enables one to change the intensity of the lines as required. Once a convenient crystal orientation is found, it can be locked reliably in that position. Since both translation and rotation of the sample are independent, incidental changes in intensities and line position due to rotation are avoided when adjusting the depth of crystal insertion. A similar construction has been described by Thompson and Waugh (1965).

2. Methodology

One of the major advantages of ruby as a material for adjacent reference samples is the high anisotropy of its signal. This makes it possible to place the relatively narrow reference lines into almost any position in the spectrum. Ruby is aluminum oxide dilutely substituted with chromium(3+) at aluminum sites. The chromium ions occupy axially symmetric (trigonal) sites with the symmetry axis parallel to the crystallographic c-axis. There is no site splitting. The spin Hamiltonian parameters of the chromium(3^+) signal are: $g_{11} = 1.9817$, $g_\perp = 1.9819$, and $b_2^0 = 0.1917$ cm^{-1} (Chang et al., 1978). The fairly strong fine structure interaction of the three unpaired electrons results in a highly anisotropic signal. Due to the axial symmetry, the line positions at any crystal orientation are solely determined by the angle between the externally applied magnetic field vector and the c-axis of the single crystal. Fig. 3 demonstrates that many angle ranges avoid overlap between the chromium and alanine lines. At the same time, there are several possibilities (at angles $<10^\circ$, around 35° and 65°) to put a ruby line as close to the alanine signal as desired if one

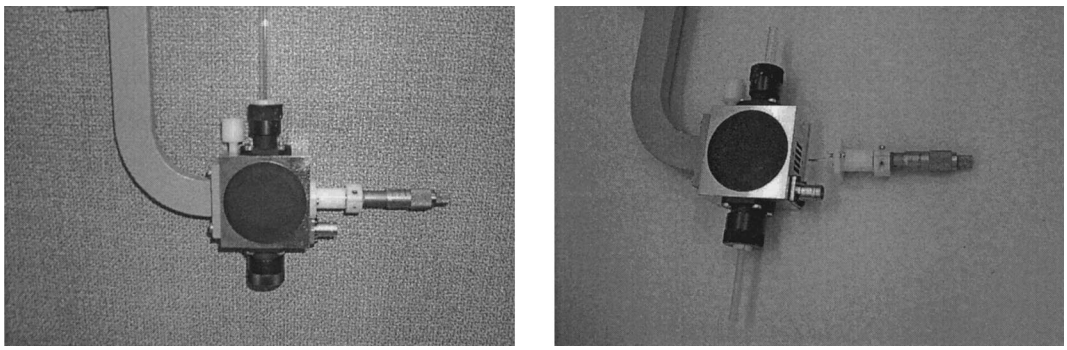

Fig. 2. Adjacent reference sample device manufactured by Bruker Instruments. Left: Assembled cavity with the reference sample device attached and quartz holder for alanine pellets. Right: The same construction in the disassembled form; the dark ruby rod and the illumination grid used for its insertion can be seen.

wants to record the two signals in the same sweep. It should be noted that shifts of the lines in the spectrum due to a change in the crystal orientation are generally accompanied by changes in their intensity, even though these changes are not always very noticeable. Hence, an adjustment of line position in the middle of a measurement series (if absolutely necessary) generally requires a careful calibration to establish the appropriate correction factor.

Modern automated spectrometers make it unnecessary to have a reference line in the same spectrum sweep as the signal of the test sample. An automation routine can be used to measure the intensity of the alanine and a remote ruby line in separate sequential scans. Thus, we normally use a line located at 220 mT at crystal orientation with $\theta \approx 28^{\circ}$. In order to allow the spectrometer and signal to stabilize after the field jump between sequential scans (particularly when using long time constant), a pre-acquisition delay of a few seconds is added in the automation routine to avoid signal distortion.

The dependence of ruby signal intensity on the depth of the crystal insertion is shown in Fig. 4. The curve reflects the passage of the crystal through the area of the strong microwave magnetic field near the cavity wall. (When a sample is located in the vicinity of the cavity wall, the signal phase is opposite to the signal phase in the cavity center due to the sample position with respect to modulation coils). An important point is that, due to the length of the ruby crystal, which is extended along the direction of its movement, the maximum dependence shown in Fig. 4 is not very sharp. This weak positional dependence, in combination with the high precision of the micrometer screw, ensures a very good reproducibility of the ruby signal intensity after crystal repositioning. The relative standard deviation (RSD) of the replicate amplitudes was 0.065% for 10 spectrum recordings separated by the crystal withdrawals/reinsertions, whereas the RSD of the amplitudes of the signals recorded repeatedly with immobile ruby crystal was 0.020%. (Both sets of experiments were performed within a 10-min period on a Bruker ECS106 with the spectrometer equipped with a 4103TM cavity.) As RSDs of the EPR signals of an alanine dosimeter recorded at different pellet orientations are usually in the 0.4–0.7% range, this level of reproducibility is more than sufficient for reliably repositioning the ruby standard without a significant contribution to the dose error, if the standard has to be temporarily withdrawn from the cavity.

It is well known that a favorably strong magnetic microwave field occurs not only at the wall of the microwave cavity, but also near its center and, in principle, the ruby crystal could be placed there as well. Its signal would be even stronger because of the higher modulation amplitude in that area. However, wall position is superior to the near-central position in two respects. First, the area with the largest and most homogeneous microwave magnetic field in the center is already occupied by the dosimeter. So, it would not be possible to take advantage of the low field gradient that provided the broad maximum in Fig. 4 and,

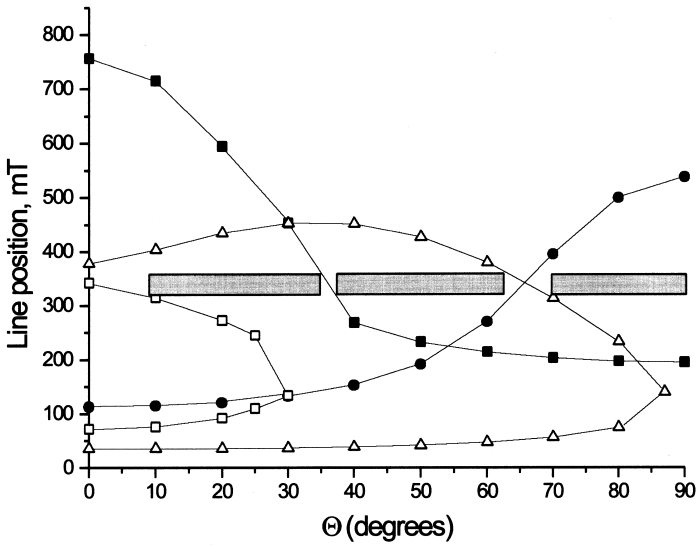

Fig. 3. Dependence of the positions of Cr(3+) lines in the X-band EPR spectrum of ruby single crystal on the angle between the crystallographic *c*-axis and the externally applied magnetic field. Frequency: 9.500 GHz, room temperature. Grey rectangles show crystal orientations at which the alanine signal range is free of ruby lines. (Points of different shapes correspond to transitions between different spin states; see Chang et al. (1978) for details).

hence, a good reinsertion reproducibility. Second, the crystal holder running through the intermediate area of strong electric microwave field would noticeably decrease the Q-factor, which may be significant in dealing with weak alanine signals in the case of low doses or thin alanine films.

As mentioned above, the response of the adjacent reference sample and the test sample to varying conditions must be the same or very similar in order to achieve a successful correction. In alanine dosimetry, one of the main sources of measurement variation is a change in the effective microwave power incident on the alanine pellets, which can vary significantly due to different moisture content among the dosimeters. Fig. 5 illustrates this point schematically. Suppose the calibration curve was constructed with dry alanine pellets that had been stored in a desiccator and the effective microwave power in them was P_1. If the test pellets were stored at a higher humidity, the effective microwave power in them, P_2, will be lower due to a lower Q value. In the worst-case scenario with no adjacent reference sample in use (Fig. 5, top), the test pellets will produce a weaker signal at the same radical concentration (dose). The degree of the decrease will depend on the shape of the $A = f(P^{1/2})$ curve, and this decrease will directly contribute to the error in the determined dose. Now, suppose that an adjacent reference sample has been used, but its saturation curve is not proportional to the saturation curve of alanine in the power range in question (Fig. 5, middle). A shift from P_2 to P_1 will cause both the signals to decrease, but, because the power dependences are not proportional to each other, the correction will not be perfect. The quality of the correction will depend on how close to proportionality the two curves are. However, if the measurements are performed in the range of proportionality of the two curves (Fig. 5, bottom), the correction will theoretically be perfect.

Fig. 6 shows the saturation curves for the ruby and alanine signals. It can be seen that the ruby signal is much more difficult to saturate and the upper limit of the proportionality range (linear in this case) is, thus, determined by the upper limit of linearity of the alanine response. A careful statistical analysis based on the comparison of the scatter of replicate signals recorded at the same power with deviations of the mean signals of such groups from the linear fit (Nagy, 2000) demonstrates that the dependence is actually linear only in the 0–0.25 mW range (that is, up to $P^{1/2} = 0.5$; this result is also in agreement with the conclusion of Wieser and Girzikowski (1996)). If measurements are performed at a power below this threshold, the most favorable situation represented in the bottom portion of Fig. 6 occurs and using the reference signal should theoretically fully compensate for power variations.

In the high-dose range, which is the main area of application of alanine dosimetry at present, the alanine signals are very strong and decreasing microwave power down to 0.25 mW does not deteriorate the signal-to-noise ratio to any noticeable degree. This is also largely true even for the 10–100 Gy range used in calibrating therapeutical sources. The only area where low microwave power may be undesirable is dosimetry with thin alanine films that typically exhibit weaker signals. However, even in this unfavorable case, high microwave power is a relatively ineffective way to improve the signal-to-noise ratio because, even in the linear range, the signal increases only with the square root of the microwave power.

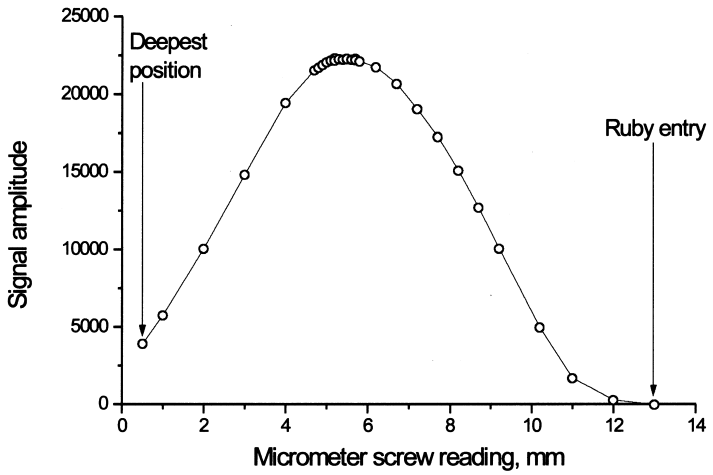

Fig. 4. Dependence of the amplitude of the ruby line at 220 mT on the readings of the micrometer screw of the ruby holder. Bruker cavity 4103TM with the standard quartz tube for alanine pellets (O. D. 7 mm; I. D. 5 mm).

Considerations regarding the proportionality of the two responses are also applicable to fluctuations in modulation amplitude, although significant variations of this parameter, apparently, are less common than variations of the effective microwave power via Q-factor. The highest signal-to-noise ratio for alanine is achieved at modulation amplitude settings in the range 1.4–1.8 mT, depending on the dose, the microwave power and the dosimeter shape (the latter determines the average modulation amplitude over the dosimeter

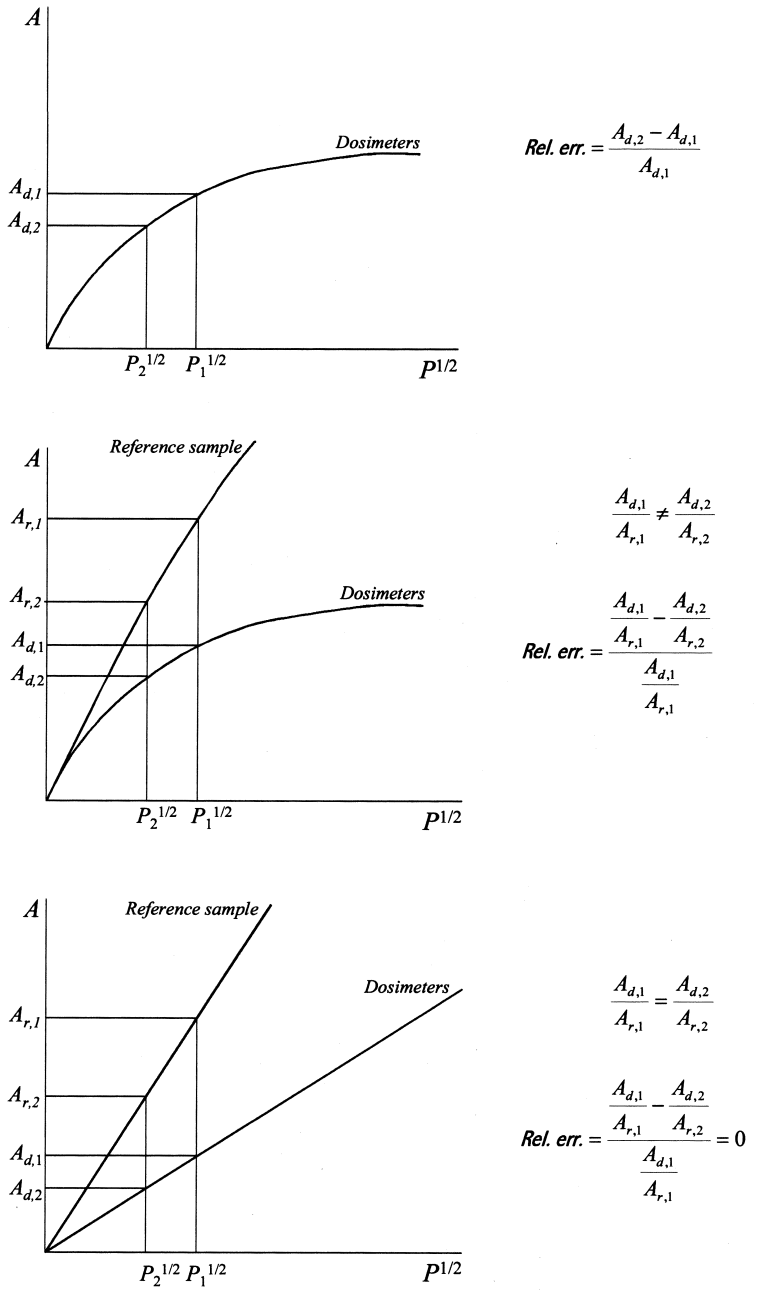

Fig. 5. Magnitude of the errors due to microwave power variations. Top: No adjacent reference sample used; no correction for signal change as a result of the power decrease from P_1 to P_2. Middle: An adjacent reference sample is used, but the signals are partly saturated; a partial correction for the power decrease. Bottom: The power is low enough, so that none of the signals is saturated; a perfect correction for the power decrease.

shape). However, heating of the cavity and its contents by the modulation coils is very significant at such high modulation amplitudes. A dosimeter requires several minutes to come to thermal equilibrium and thus to produce a stable EPR signal. Of course, the magnitude of this effect depends somewhat on the cavity type, design of the dosimeter holder, gas flow, etc. For our 4103TM cavity with its illumination grid sealed, and using a quartz tube dosimeter holder with 1-mm-thick walls and both ends open, the maximum modulation amplitude providing a stable alanine signal was 0.28 mT.

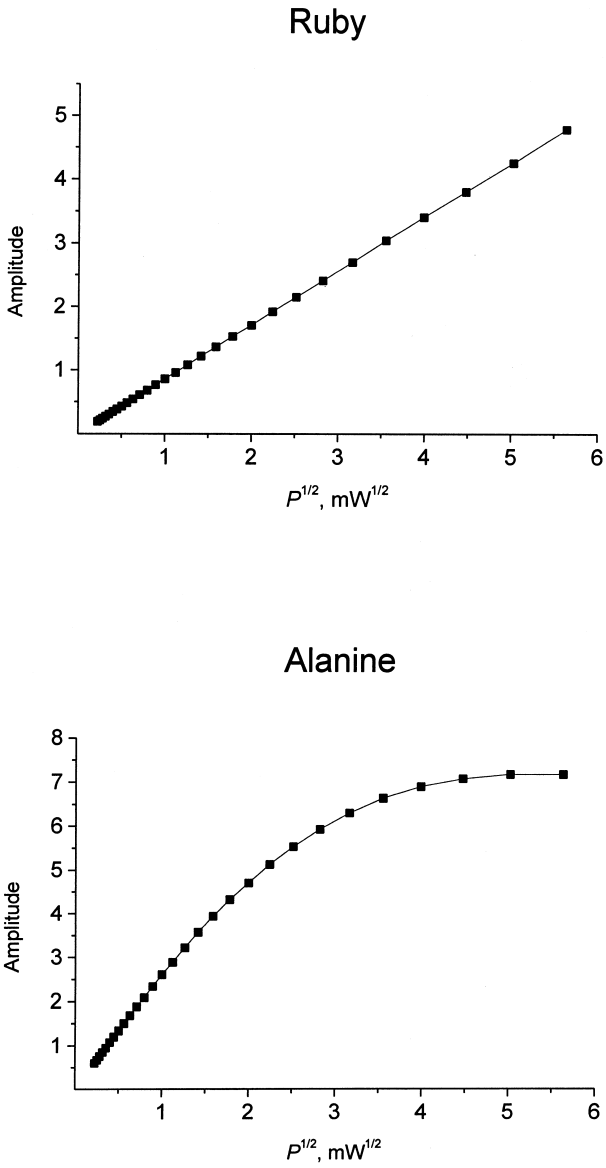

Fig. 6. Dependence of the amplitudes of the signals of the ruby reference sample and alanine on microwave power. ECS106, cavity 4103TM with the standard quartz tube for dosimeters; the ruby crystal is located near the front wall.

The amplitude dependence of the ruby line located at 220 mT at our crystal orientation (linewidth 4.5 mT) on modulation amplitude is linear within the measurement uncertainties up to 0.6 mT, whereas nonlinearity in the alanine response is already noticeable at a modulation amplitude of 0.28 mT (Fig. 7). Fitting the experimental dependence with an analytical function in the range of interest (see Fig. 7), one can calculate the errors that would occur if the modulation amplitude were to deviate from the preset optimal value of 0.28 mT (Table 1). Although normalizing the alanine signal to ruby does not correct the error in full because of the nonproportionality of the responses, it decreases the error by approximately a factor of six. These results are, in fact, for the worst-case scenario, namely, for the case of the low dose of 0.1 kGy. For that case, the spin–spin interactions are weak, the spectral line is not broadened significantly and the curvature of the amplitude dependence on modulation amplitude is, therefore, the largest. For the more commonly measured doses above 10 kGy, which produce broader spectral lines, the residual error of the ruby-corrected signal will actually be smaller. Even though the responses of the alanine and ruby signals are not strictly proportional between 0.2 and 0.3 mT, this range offers optimal results for the following reasons: the probability of significant variations of modulation amplitude during measurements is small, partial correction of the resultant errors by means of the ruby signal is fairly good and using a modulation amplitude in the alanine linear range would result in about a 10-fold decrease in the alanine signal from its maximal value.

Use of an adjacent standard is based on the assumption that the distribution of the microwave fields in the cavity remains unchanged during the measurements. One of the possible causes of field distribution changes is rotation of the quartz tube holder containing the dosimeter in order to obtain spectra at different pellet orientations. For example, at NIST, each pellet is measured at two mutually perpendicular orientations with respect to the externally applied magnetic field, and the dosimeter response is calculated as the mean of the two ruby-normalized alanine amplitudes. However, no quartz tube holder is absolutely perfect in terms of the uniformity of wall thickness and concentricity. As a result, the ruby signal slightly varies with different orientations of the holder because the microwave magnetic field at the ruby sample varies. If this effect is not taken into account, normalization to ruby, while correcting results for spectrometer instability and Q-factor variations, will always contribute to the error in the signal value and, consequently, the dose

measurement. In order to minimize this error, one should investigate the dependence of ruby amplitude on tube orientation and select orientations that produce approximately the same ruby signal. Results of such a study for our sample tube are shown in Fig. 8. The two mutually perpendicular orientations 2 and 8 provide the average difference in the ruby amplitudes of only 0.0175%, which is good enough for alanine dosimetry purposes, and these two orientations are now routinely used in the NIST dosimetry practice. Table 2 lists typical differences in the ruby signal amplitudes in the course of a typical dosimetric experiment. As can be seen, in most cases, the contribution to the total error from the difference in the microwave field distribution does not exceed 0.1%, which can be regarded as negligible in comparison with the contribution from the alanine signal anisotropy.

An important feature of the device described here is its suitability for "single" cavities. An alternative strategy could be using a dual (H_{104} mode) cavity with a reference sample permanently residing in one chamber and the test samples replaced consecutively in the other. Although such an arrangement would serve in the same way as our device in many respects, it has one significant drawback. One switches from one chamber to another by turning off one set of modu-

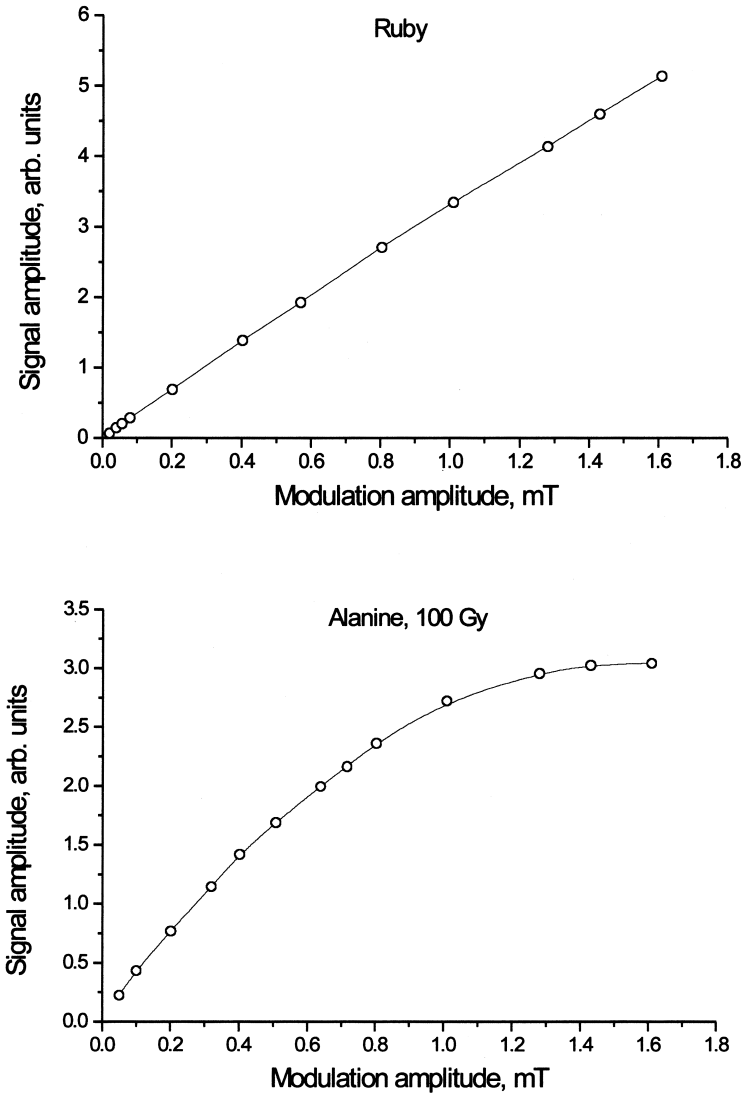

Fig. 7. Dependence of the amplitudes of ruby and alanine signals on modulation amplitude. Least-squares fit for the alanine dependence in the range 0.05–0.8 mT: $Y = 0.474 + 3.877x - 1.252x^2 + 0.000413x/\ln x$; standard error of the fit is 0.012.

Table 1
Errors in absolute and ruby-normalized alanine signal amplitudes due to deviations in modulation amplitude from the preset optimal value of 0.28 mT. Bruker pellets, dose 100 G_y, microwave power 0.25 mW

Deviation of modulation amplitude (mT)	Error without ruby standard correction (%)	Error after ruby standard correction (%)
−0.05	−15.6	2.6
−0.04	−12.5	2.1
−0.03	−9.3	1.5
−0.02	−6.2	1.0
−0.01	−3.1	0.5
0.00	0.0	0.0
0.01	3.1	−0.5
0.02	6.1	−1.0
0.03	9.1	−1.5
0.04	12.1	−2.0
0.05	15.0	−2.4

lation coils and turning on another set of coils. This keeps the system in a permanent state of thermal instability and adversely affects the reproducibility of the results. Our tests have shown that, other conditions being equal, the reproducibility attainable with a dual cavity is at least a factor of two worse than the reproducibility that can be achieved with a single cavity.

It is important to note that this paper is devoted to an intensity and not to a concentration standard. The number of paramagnetic centers in the adjacent reference sample is not known and even if it were, it could not be used in quantitations directly, because the reference sample is in a different modulation and microwave field than the unknown sample. As the intensity of an EPR signal is proportional to the modulation amplitude and to the amplitude of the microwave magnetic field squared, the ratio of signals from these samples does not represent the ratio of the numbers of paramagnetic centers in them and cannot be used directly for quantifying the unknown. A special calibration would be necessary to correct for the differences in the magnetic field amplitudes. Differences in the shapes of the reference and test samples must also be taken into account (Nagy and Placek, 1992).

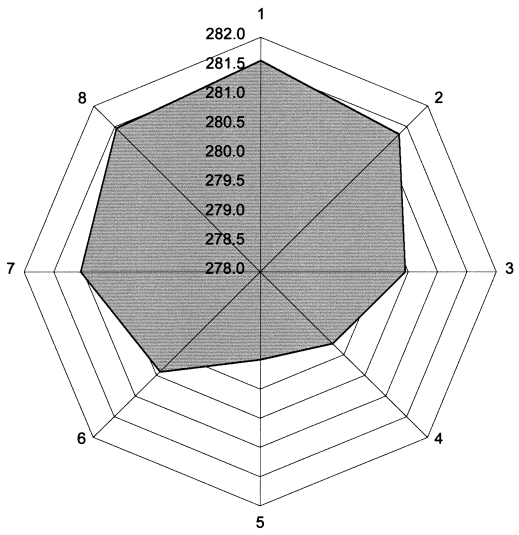

Fig. 8. Dependence of the ruby signal amplitude on the orientation of a quartz tube holder in a 4103TM cavity. Polar coordinates are used: numbers 1–8 designate eight tube orientations spaced by 45° the radial distance from the center shows the ruby signal amplitude.

3. Benefits

We will illustrate the advantages of using the adja-

Table 2
Variations in the adjacent ruby standard amplitudes at two mutually perpendicular orientations of the quartz holder with an alanine dosimeter

Dosimeter no.	Difference in ruby signals (%)
1	0.02
2	0.01
3	0.13
4	0.10
5	0.01
6	0.08
7	0.04
8	0.02
9	0.01
10	0.06
11	0.01
12	0.10
13	0.07
14	0.01
15	0.08

cent reference sample technique with a few examples. First, using such a reference makes it possible to detect and investigate minute changes of signals with time, which are very difficult to detect otherwise because of comparable or larger variations in the sensitivity of EPR spectrometers. Fig. 9 shows typical examples from our study of alanine signal evolution in the first days after irradiation. Signal changes are very small (the range of their variations is usually below 1%) and they cannot be reliably elucidated or even detected without an adjacent reference sample (see the top graphs in Fig. 9). Since the ruby signal recorded immediately before or after each recording of the alanine signal is affected by the variations of the spectrometer

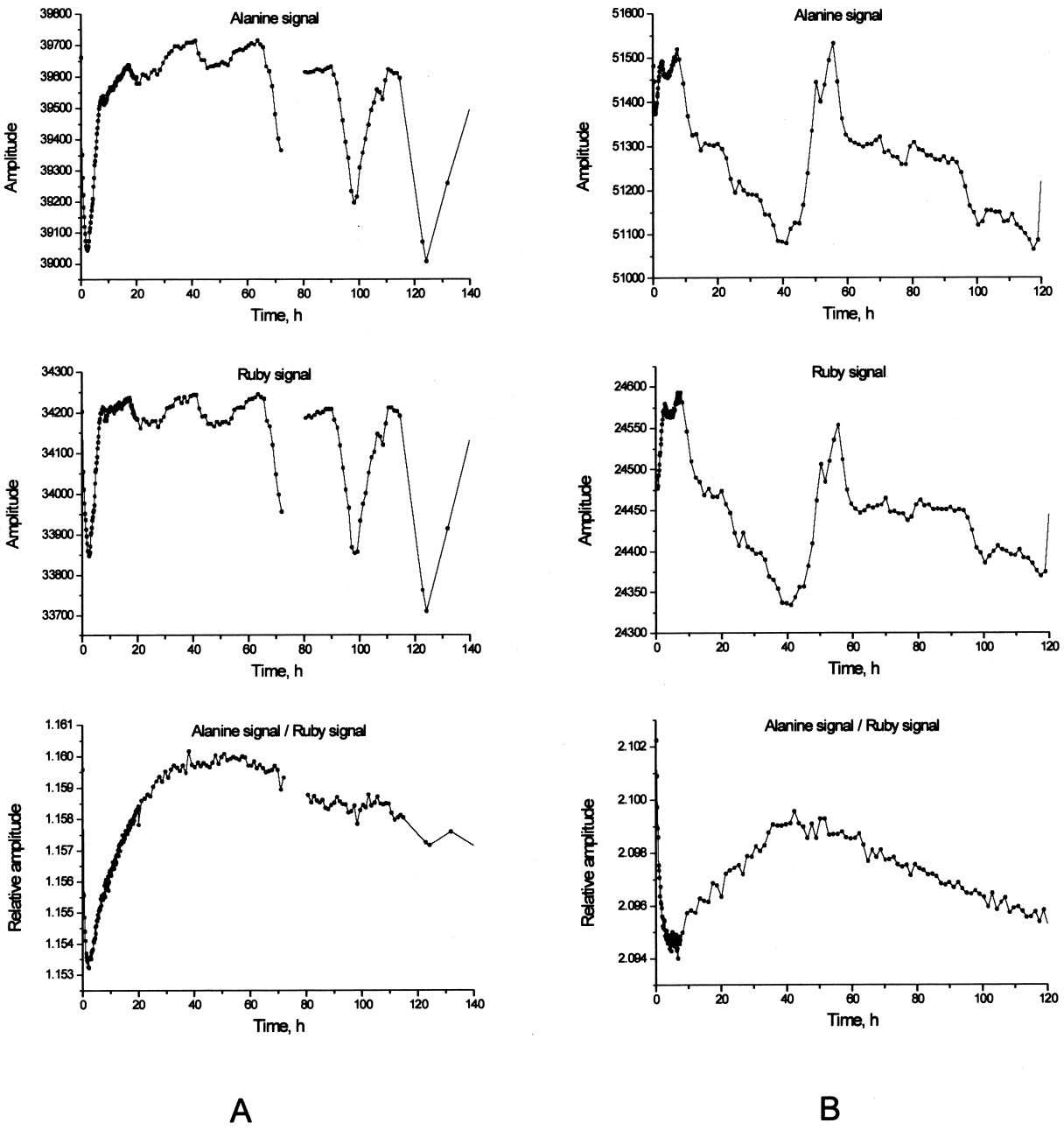

Fig. 9. Effect of normalization to the signal of the adjacent ruby reference sample in studying evolution of the alanine signal after ^{60}Co gamma irradiation. *A* 50 kGy; *B* 100 kGy.

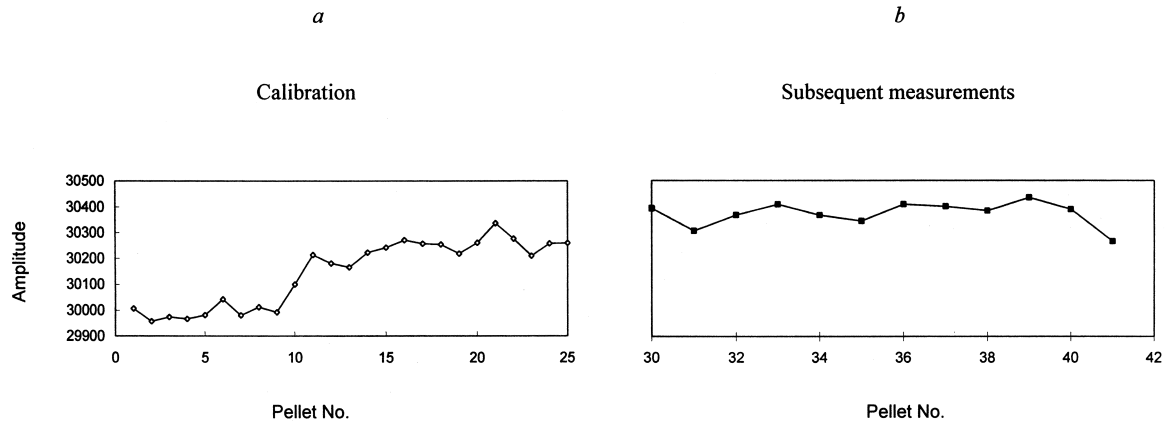

Fig. 10. Amplitudes of the signals of a ruby adjacent reference sample in the course of dose measurements for a custom source calibration. The pellet numbers show the order of recording the spectra.

sensitivity approximately in the same way as the alanine signal (middle graphs in Fig. 9), their ratio turns out to be almost independent of the spectrometer sensitivity and characterizes the real evolution of the alanine signal (the bottom graphs in Fig. 9). It can be seen from Section A of Fig. 9 that normalizing to the ruby signal decreases the scatter of points down to one hundredth of a percent, making it at least an order of magnitude smaller than it would be without use of an adjacent reference sample. It was only due to the adjacent reference sample that we were able to investigate short-term changes of the amplitude of the alanine signal systematically (Nagy and Desrosiers, 1996).

Accurate monitoring of the spectrometer sensitivity is also very useful in routine dose measurements. Fig. 10 shows ruby signal amplitudes recorded after recording the signal of each alanine pellet during a typical custom source calibration. One can see that a significant jump in the spectrometer sensitivity occurred in the middle of constructing the calibration curve and the sensitivity kept slightly increasing subsequently (Fig. 10a). The signals of the test pellets (Fig. 10b) were thus recorded under conditions of enhanced sensitivity. Furthermore, the test pellet doses corresponded to the part of the calibration curve covered by Pellets 1–9 that were recorded under con-

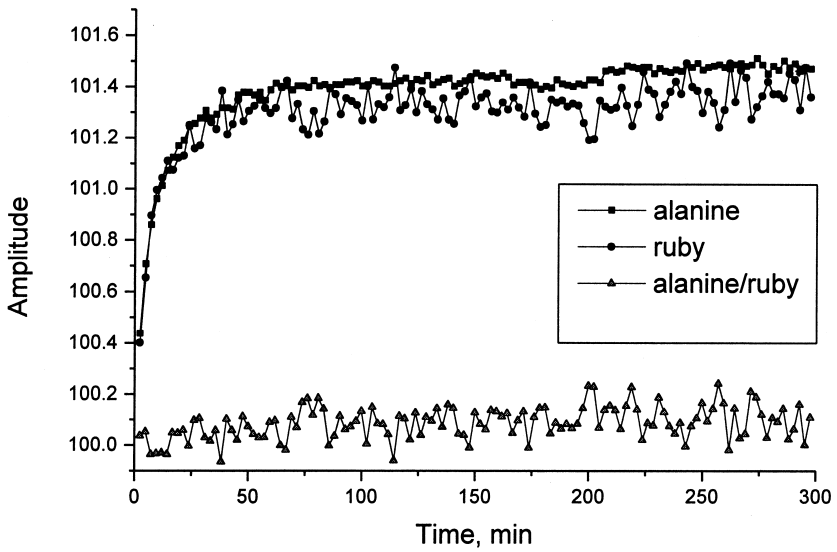

Fig. 11. Changes in the amplitudes of alanine and ruby signals, as well as in their ratio, for a dosimeter just brought in from an environment with a relative humidity higher than the humidity of the EPR laboratory.

ditions of "low-sensitivity" (Fig. 10a). The adjacent reference sample corrected for this discrepancy in recording conditions; if it had not been used, the doses would be overestimated by about 1%. Normalization of each alanine signal to the ruby signal made it possible to avoid this significant error. The widely used technique of checking the spectrometer sensitivity before or/and after the measurement session by recording a spectrum of a "standard" alanine dosimeter cannot make such corrections as accurately as reference sample signals recorded immediately after recording the alanine dosimeter signals.

Normalization to ruby helped us to investigate the temperature dependence of the alanine signal (Nagy et al., 2000) much more accurately than it was possible before. Changes in the alanine signal with irradiation temperature are very small, and the large number of measurements necessary for statistically significant results take a long time. During this period, the sensitivity of the spectrometer can vary over a range comparable to or greater than the range of temperature-dependent changes. Normalization to ruby made it possible to determine the alanine temperature coefficients accurately and, in particular, to reveal their non-monotonic dependence on the dose (Nagy et al., 2000), which was overlooked in numerous studies before. An adjacent reference sample is even more important when one needs to monitor small changes of a signal over long periods of time, as in studies of long-term fading of the alanine signal. Using the ruby reference sample we could consistently measure signals of alanine pellets that were stored under different conditions for a period of about 1 year to study their changes (Sleptchonok et al., 2000). The measurements of each signal were performed twice a week and the uncertainty of the measurements was below 1% (2σ).

As already mentioned, a very important function of an adjacent reference sample is to correct dosimeter signals for variations in the cavity Q-factor. This aspect is discussed in detail by Sleptchonok et al. (2000). As a brief illustration, Fig. 11 shows changes in the signals of alanine and ruby, as well as in their ratio, for a pellet just removed from an environment with a relative humidity higher than the relative humidity in the laboratory. The alanine signal increases by about 1% due to the dosimeter drying. Accordingly, so does the amplitude of the ruby signal. This occurs because both are proportional to the cavity Q-factor, which is dependent on the moisture content in the cavity and the samples. Therefore, the ratio of the amplitudes remains constant within 0.1%. This shows that normalizing alanine signals to the ruby signal makes it possible to compare accurately the signals from pellets of different moisture contents, which is essential for precise dosimetry.

4. Limitations

The above examples demonstrate that using an adjacent reference sample makes it possible to substantially increase the accuracy of alanine dosimetry in several ways. However, there are certain restrictions. One of them is due to the fact that the alanine and reference signals are not recorded simultaneously, but immedi-

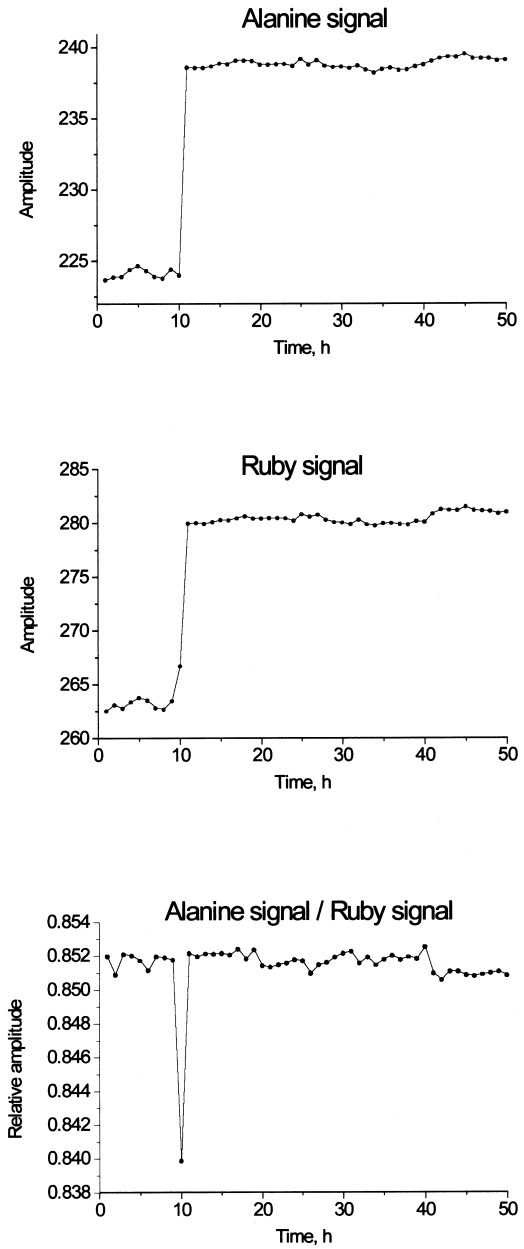

Fig. 12. Incomplete correction in the case of a very sharp change in the spectrometer sensitivity.

ately one after the other. This means that a very sharp change in the spectrometer sensitivity may not be corrected in full. Such a situation occurred during the measurements represented in Fig. 12.

Another limitation is related to microwave field perturbation effects. Corrections for Q-factor variations are based on the assumption that varying moisture content of dosimeters changes amplitudes of the microwave field *proportionally* over the whole cavity. This is not absolutely correct. Introduction of water (or any other high dielectric constant material) into a cavity, also produces changes in the microwave magnetic field distribution, causing the effect known as microwave field perturbation. The magnitude of the perturbation effect under conditions of alanine dosimetry is very difficult to calculate theoretically for a number of reasons. However, estimations based on theoretical calculations for simpler cases (Nagy, 1994) suggest that this effect should be very small in comparison with the errors eliminated by the adjacent standard technique. In fact, experimental data (Sleptchonok et al., 2000) demonstrate that normalization to the ruby signal cannot fully correct Q-factor variations only in the extreme case of measuring the signal of a dosimeter that just arrived to the EPR lab from an environment with 94% relative humidity. Under milder conditions, including 75% relative humidity, the correction was quite satisfactory.

The third difficulty, the reason for which is not quite clear to us at the moment, is associated with accidental abnormal shutdowns of the EPR spectrometer due to power failures or similar mishaps. After the spectrometer is turned on again after such events (even immediately), the ratio of the alanine and ruby amplitudes may differ from the previous value by as much as 1%, and it takes the ratio several days to return to its original value. This phenomenon was observed two or three times a year on only one of our spectrometers (ECS106) and may be limited to this particular machine.

5. Conclusion

The 40-year-old technique of using adjacent reference samples proves to be very useful for alanine dosimetry. It has obvious advantages over the other reference techniques that are currently utilized and is recommended for more extensive use in the future.

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