ESR DOSIMETRY

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Abstract — The demonstration 30 years ago that the amino acid, alanine, could serve as a solid dosimeter by electron spin resonance (ESR) spectrometry, has led to a fascinating success story. Radiation-induced paramagnetic centres, the de-aminated free radicals associated with unpaired electrons, are stable during and after irradiation. The free radical concentration proportional to the absorbed dose can be measured as the main peak-to-peak amplitude of the first derivative of the ESR absorption spectrum. In addition to alanine, other solids (e.g. certain sugars and polymers, quartz, bone) may be used to cover a broad range of absorbed doses 10⁻⁶ to 10² Gy. Indeed, efforts proceed to improve the sensitivity, accuracy, and precision of ESR dosimetry. Advantages include the ability to simulate biological tissues in terms of radiation absorption properties, small size (e.g. thin films and small pellets), the possibility of in vivo dosimetry, ruggedness, stability, and resistance to environmental and dose rate effects.

INTRODUCTION

Since the early work by Box and Freund in 1959¹ and Brashaw et al. in 1962², Röntgen and Simmons in 1963³, and Bernant et al. in 1971⁴, the development of alanine/ESR dosimetry has reached a level that makes it competitive with classical methods of dosimetry such as thermoluminescence, chemical (e.g. Fricke) and ionisation methods, at least at the higher dose ranges, 10⁻¹⁰ to 10⁴ Gy. In particular, the work of Regulla and colleagues⁵ at the Gesellschaft für Strahlen- und Umweltforschung (GSF) in Neuherberg/Munich has resulted in a widely used dosimetry system based on ESR analysis of microcrystalline L-α alanine

\[ \text{NH}_2 \quad \bigg| \quad \text{CH}_2 - \text{CH} - \text{COOH} \]

which, upon irradiation, is de-aminated to the radical CH₃₂CH₂⁻COOH. The alanine dosimeter usually consists of finely dispersed microcrystals suspended uniformly at concentrations as high as 95% by weight in a polymeric binder, such as high temperature melting paraffin, low molecular weight polyolefins (e.g. polyethylene, polyethylene-propylene, polyethylene), vinyl polymers (e.g. polyvinyl pyrrolidone, polyethylene-vinyl acetate copolymers, silicones, and low ESR signal epoxies, wax or paint. Figure 1 shows a photograph illustrating the various shapes and sizes of alanine dosimeters currently in use, including rods, pellets, flexible films, and cables that are extruded, pill pressed, or mould formed. The cable can be cut to suitable lengths for analysis in the cavity of an ESR spectrometer⁶.

The aim of this work is to review the state-of-the-art and to report on recent advances in materials, analytical methods, and dosimetry applications. Tables 1 and 2 list key ESR dosimeter types, constituents, binder substances, shapes, dose ranges, and a sample reference for each. At present, several manufacturers supply sophisticated, high quality ESR spectrometers, and some are adding simpler, less expensive, compact instruments dedicated to dosimetry applications⁷. There are also efforts underway to mass produce dosimeter pellets, rods, or films of alanine in binder materials having a negligible background ESR signal. It may, in fact, be

Figure 1. Several forms of alanine-ESR dosimeters from different countries including rods, pellets, films and cable materials, all of which are L-α alanine powder, shaped or extruded in suspension with a polymeric binder (courtesy of M. P. Desrosiers, NIST).
possible to supply for dosimetry a solid, e.g. a radiation sensitive polymer or solid state crystalline material, that requires no binder. Other analyses can also be used with alanine for dosimetry, such as spectrophotometry of radiation oxidised transition metal (Fe) complexes with dyes (xylol orange) in aqueous alanine solutions (dose range $10^4$–$10^6$ Gy$^{25-31}$), or electrochemical potentiometry by ion selective electrode analysis of the concentration of [NH$_2$] when irradiated alanine is dissolved in water (dose range $10^5$–$10^6$ Gy$^{25-34}$).

**ESR SPECTROMETRY**

When the pairing of electrons of a molecular substance is disrupted by radiation-induced free radical formation, and the unpaired spins are stable (as in many solids), the resulting paramagnetic absorption intensity is proportional to absorbed dose and is measurable under normal laboratory conditions in an ESR spectrometer. The conventional spectrometer is described in detail in the literature$^{29}$ and, in simplest terms, consists of a dipole electromagnet with a cavity operated at microwave frequencies (X band typically at 9.6 GHz frequency, with the external static field modulated by an RF field at 100 kHz). By sweeping the static magnetic field applied to the resonant cavity of an X band spectrometer carrying a constant microwave frequency, the

<table>
<thead>
<tr>
<th>Dosemeter material</th>
<th>Formula</th>
<th>Binder material</th>
<th>Form</th>
<th>Dose range (Gy)</th>
<th>Sample reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-α alanine</td>
<td>C$_2$H$_4$NO$_2$</td>
<td>polymer (e.g. polyethylene)</td>
<td>rods, pellets, films</td>
<td>$5 - 10^5$</td>
<td>(6)</td>
</tr>
<tr>
<td>D-α sucrose</td>
<td>C$_2$H$<em>2$O$</em>{11}$</td>
<td>–</td>
<td>pellets, powder</td>
<td>$5 - 10^4$</td>
<td>(11)</td>
</tr>
<tr>
<td>D-α lactose (mononohydrate)</td>
<td>C$_2$H$<em>2$O$</em>{11}$H$_2$O</td>
<td>–</td>
<td>pellets, powder</td>
<td>$10^3 - 10^4$</td>
<td>(12)</td>
</tr>
<tr>
<td>D-α glucose</td>
<td>C$_2$H$_2$O$_6$</td>
<td>–</td>
<td>pellets, powder</td>
<td>$10^3 - 10^4$</td>
<td>(13)</td>
</tr>
<tr>
<td>D-α mannose</td>
<td>C$_2$H$_2$O$_6$</td>
<td>–</td>
<td>pellets</td>
<td>$5 - 10^4$</td>
<td>(14)</td>
</tr>
<tr>
<td>Tris(hydroxymethyl)aminomethane</td>
<td>C$_2$H$_6$NO$_3$</td>
<td>–</td>
<td>pellets, powder</td>
<td>$5 - 10^4$</td>
<td>(14)</td>
</tr>
<tr>
<td>Methyl viologen</td>
<td>C$_2$H$_4$N$_2$</td>
<td>polyvinyl alcohol</td>
<td>films</td>
<td>$10^3 - 3 	imes 10^5$</td>
<td>(15)</td>
</tr>
<tr>
<td>Metallo-diphalocyanines</td>
<td>C$<em>{30}$H$</em>{30}$N$_{10}$</td>
<td>Hf, Lu, Zr</td>
<td>ethanol, chloroform</td>
<td>organic solution</td>
<td>$2 - 10^3$</td>
</tr>
<tr>
<td>Triphenylmethane dyes</td>
<td>C$<em>{20}$H$</em>{18}$N$_4$</td>
<td>–</td>
<td>polyvinyl butyral</td>
<td>films</td>
<td>$10^3 - 10^4$</td>
</tr>
<tr>
<td>Cellulose</td>
<td>(C$_6$H$_5$O$_9$)$_n$</td>
<td>–</td>
<td>wafers, films</td>
<td>$10^3 - 5 	imes 10^4$</td>
<td>(18)</td>
</tr>
<tr>
<td>Polyvinyl alcohol</td>
<td>(C$_2$H$_4$O)$_n$</td>
<td>–</td>
<td>powder</td>
<td>$10 - 10^4$</td>
<td>(19)</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td>(C$_2$F$_4$)$_n$</td>
<td>–</td>
<td>rods, films</td>
<td>$10^3 - 10^4$</td>
<td>(20)</td>
</tr>
</tbody>
</table>

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<tr>
<td>Quartz</td>
<td>SiO$_2$</td>
<td>glass powder</td>
<td>$10^4 - 10^5$</td>
<td>(21)</td>
</tr>
<tr>
<td>Magnesium orthosilicate</td>
<td>Mg$_2$SiO$_4$·Tb</td>
<td>powder</td>
<td>$5 - 3 	imes 10^3$</td>
<td>(22)</td>
</tr>
<tr>
<td>Magnesium sulphate</td>
<td>MgSO$_4$</td>
<td>powder</td>
<td>$1 - 10^5$</td>
<td>(23)</td>
</tr>
<tr>
<td>Lithium fluoride</td>
<td>LiF·Mg·Tl</td>
<td>powder</td>
<td>$10^4 - 10^5$</td>
<td>(24)</td>
</tr>
<tr>
<td>Bone (hydroxyapatite)</td>
<td>Ca$_{10}$H$_2$(OH)$_2$(PO$_4$)$_6$</td>
<td>powder</td>
<td>$10^4 - 10^5$</td>
<td>(25)</td>
</tr>
<tr>
<td>Dental enamel</td>
<td>(tribasic)</td>
<td>solid pieces</td>
<td>$10^4 - 10^5$</td>
<td>(26)</td>
</tr>
</tbody>
</table>
gyromagnetic properties of the paramagnetic material can be evaluated in terms of the splitting of Zeeman energy states (electron spin states $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$). In a simple free electron system, the high frequency magnetic field $B_1$ at right angles to the static field $B_0$ induces permitted magnetic dipole transitions ($\Delta m_s = 1$) between the energy levels, which satisfy the resonant condition

$$\Delta W = h\nu = g\mu_B B_0$$

The product of Planck's constant, $h$, and the selected frequency, $\nu$, is such that the energy level separation, $\Delta W$, gives a characteristic peak (or peaks) in paramagnetic absorption at given values of the swept magnetic field strength, $B_0$. For most hydrocarbons and some ordered inorganic solids, there is, at a value of $B_0$, an associated dimensionless Landé spectroscopic splitting factor ($g$) according to the effects of chemical shifts on the angular momentum of the electron (most organic free radicals have a $g$ factor near a value of 2). $\mu_B$ is a constant, the Bohr magneton ($\mu_B = 9.2741 \times 10^{-23}$ JT$^{-1}$). The value of $g_B$ for a free electron is 2.00232.

In ESR analysis, since the separation $\Delta W$ increases linearly with the value of $B_0$, the sweep of the magnetic field in a sample held in the microwave cavity encounters characteristic absorption peaks at resonance values of $B_0$. The resonances are detected by a microwave rectifier (silicon crystal) held at a given bias current, with absorption intensities depending on the concentration of unpaired spins in the sample. Each type of free radical (or transition metal ion, excited triplet state of a diamagnetic molecule, radical ion or ion pair, or solid state defect) has a representative absorption spectrum, which for most applications is displayed as the first derivative of the normalised absorption curve of detector output current relative to magnetic field strength $B$. The ESR spectrum can be relatively simple or complex, depending on the hyperfine coupling of the magnetic moment of the unpaired electron with that of the nuclei in the surrounding medium, chiefly hydrogen nuclei in the case of organic absorbers.

Typically the applied static field is modulated at a fixed radiofrequency (generally a value in the range of 50 to 100 kHz) and the magnetic field sweep usually encompasses a field scan range of tens of mT around a mean value of some hundreds of mT. The spectrometer is designed so that the magnetic field in the cavity is the oscillating $B_1$ field of the microwave, perpendicular to the applied (external) $B_0$ field from the electromagnet. Most measurements are made at room temperature, with a given quantity of the irradiated sample being held reproducibly at a fixed position in the cavity in a silica glass tube. The common data acquisition times for each sample range from seconds to minutes, with the measurement period being about 2–3 minutes, including the changing of samples.

DOSEMETER CHARACTERISTICS

Regulla and Deffner(6) give details of typical measurement conditions in the analysis of alanine dosemeters. Table 3 gives a list of steps and precautions that are required in the performance of alanine/ESR dosimetry.

Figure 2 shows, in terms of the ESR intensity relative to the magnetic field, the first derivative absorption spectra of some of the dosemeters listed in Tables 1 and 2. In each case the spectrum has smeared, multiple lines, the ‘satellite’ lines assumed to be 'spin-flip' transitions and low field, hyperfine coupling with surrounding methyl group protons(59). Any fine structure due to spin–spin interaction is poorly resolved, mainly because of anisotropy and random orientation of the bound polycrystalline medium. Figure 3 gives the response curves for the dosemeters whose ESR spectra are shown in Figure 2. It is observed that alanine is relatively sensitive to ionising radiation and can be used at doses below 10 Gy(60,62). For very high doses (10$^6$–10$^8$ Gy), pure SiO$_2$ powder may be used(23). All of these dosemeters in dry polycrystalline form show a stable ESR signal before and after irradiation, with the exception of cellulose, which is somewhat unstable during the first 48 h after irradiation, but stable thereafter.

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ESR dosimeter substances usually include microcrystalline powders, with or without a binding medium. Reproducibility depends on availability of samples matched in shape, size and the mass of the sensor material. Ideally, a commercial supply of large quantities of ESR dosimeters of a given formulation and format is needed, but this still has not happened. Current efforts are being given in several laboratories, however, to introduce such a mass produced dosimeter, such as alanine (with binder) pellets. Key requirements will be as follows:

- Replication in terms of dosimeter response characteristics.
- Ruggedness and ease of handling.
- Long shelf life and low background signal.
- High precision of response to radiation (peak-to-peak ESR signal amplitude against dose).
- Suitable packaging and convenience for calibration.
- Simulation of biological tissue (e.g. muscle), in terms of radiation absorption properties.
- Wide dynamic range, in terms of useable absorbed dose levels for broad applications.
- Low cost for individual dosimeter samples.
- Stability of ESR signal after irradiation.
- Absence of dose rate dependence of response.
- Optimum control of humidity and temperature dependence during irradiation and storage.

**ESR Dosimetry Applications**

The measurement of radiation-induced free radicals in solids by ESR spectrometry can serve a wide range of applications including the measurement of low and high LET radiation doses in clinical radiography, bone dosimetry in nuclear medicine, quality control for food irradiation and the detection of irradiated foods, validation and quality control for radiation sterilisation of medical devices and drugs, investigation of radiation accidents and emergencies (using bone, tooth enamel, ceramics, buttons, jewellery, clothing, sugar, candy, and building materials), dose mapping by thin films and microscopy by spectral-spatial three-dimensional imaging technique, measurement of radiation damage of materials and electronic components, dating of calcites, carbonates, teeth, and bone, dosimetry transfer calibration services, and dosimetry intercomparison and correlation studies. The many applications of ESR dosimetry in the dose range $1 \times 10^6 - 10^8$ Gy are well covered by recent review articles and the three international symposia on the subject. Current efforts are proceeding in

**Table 3. Means of improving alanine dosimetry precision and accuracy**

The UK National Physical Laboratory in its ‘Alanine Dosemeter Reference Service’ reports for its alanine system a random uncertainty of $\pm 1.6\%$ (95% confidence level) and an overall estimated uncertainty of $\pm 3.0\%$ (95% confidence level), in the absorbed dose range $10^2 - 4 \times 10^5$ Gy.

Sieving of L-$\alpha$ alanine (99%) microcrystals to a given size distribution.

Uniform blending of alanine with binder (typical ratio 90% alanine 10% binder by weight per cont).

Maintaining protection from ultraviolet and sunlight, and conditioning at 50% (± 10%) relative humidity.

Using a binder (e.g. paraffin, polyethylene) that protects against adverse moisture effects due to hydrophilic property of alanine.

Matching of size, shape, and mass of dosimeters in a batch.

Preconditioning heat treatment of alanine/binding system at temperatures near melting point of binder.

Sufficient warm-up of spectrometer (typically 2 h), because of possible initial RF drifting.

Careful and repetitive positioning and orientation of dosimeter samples in ESR microwave cavity.

Using low power ($< 5$ mW) in the X band spectrometer, for optimum response.

Choice of analysis of peak-to-peak amplitude (faster procedure) or double integration of the area under the spectrum (for single-line spectra only).

Repeated reading cycles (multiple scans) of each sample to improve precision.

Calibrating receiver gain settings, RF modulation amplitudes, microwave power (and frequency), and sweep time constant and scanning rate.

Constitution of detector bias current and base line setting.

Correcting for irradiation temperature dependence of alanine response; temperature coefficient is $+ 0.1\%$ to $+ 0.2\%$ per degree celsius (between $-60 \degree C$ and $+60 \degree C$), depending on the system.

Controlling of temperature during ESR reading (temperature coefficient typically $+ 0.23\%$ per degree celsius between $12 \degree C$ and $25 \degree C$).

Establishing a calibration function (ESR signal intensity against absorbed dose) for a given set of instrumental parameters.
order to expand the lower measurable dose to therapy levels (~1–5 Gy), by suppressing the background signal and looking at materials that have stable ESR signals and intrinsically greater sensitivity in terms of radiation chemical yield of stable paramagnetic centres. Another useful development is the automation of the ESR reading of dosemeter pellets for larger volume dosimetry (ESRD).

SUMMARY

The use of electron spin resonance spectroscopy for the analysis of several kinds of solid state substances has given an important method of dosimetry for applications in radiation processing of materials, radiation sterilisation of medical devices and pharmaceuticals, and the detection of certain irradiated foods. The ESR technique is beginning to be used for dosimetric studies of some radiation accidents (e.g. Chernobyl) and for radiotherapy dosimetry. The key radiation-induced species are represented by free radical concentra-

tions, which are measured in terms of the peak-to-peak amplitude of the first derivative of the ESR absorption spectrum. A functional relationship is established between this peak height and the absorbed dose in the solid state material. Some substances for dosimetry applications include the amino acid, alanine, sugars (e.g. lactose, sucrose, mannose) and hydroxyapatite in bone and tooth enamel, where measurements can be made of absorbed doses in the range $10^3$–$10^5$ Gy. To measure higher doses, it is possible to apply ESR analysis of cellulose ($10^3$–$10^5$ Gy), micro-
crystalline quartz ($10^2$–$10^5$ Gy), and certain polymers (e.g. polyvinyl alcohol, special epoxics, etc.) (up to $10^5$ Gy).

Advantages of the alanine ESR dosemeter include broad dynamic range, long-term stability, linear response, relatively high precision, non-destructive analysis, and ruggedness. One disadvantage is that although the dosemeter ingredients are inexpensive the readout instrument is very costly; nevertheless, ESR instrument suppliers are beginning to supply

![Figure 3. Radiation response curves in terms of ESR signal intensity (peak-to-peak amplitude versus absorbed dose) for the dosemeter ESR spectra shown in Figure 2.](image)
special spectrometers aimed at dosimetry at a more manageable expense. Another cause for concern is that the dosemeters themselves are not yet mass produced in large reproducible lots, which leaves it up to the users to produce alanine dosemeters themselves, or to requisition a quantity from the increasingly wide assortment of shapes and sizes now being produced for a variety of in-house applications all over the world. Perhaps with the enhanced interest in alanine as a clinical dosemeter for therapy level doses, as evidenced by the formation of an IAEA Advisory Group on this subject, wider application and availability will ensue. One recent encouraging development is the establishment of a reference calibration ESR alanine service by the UK National Physical Laboratory (NPL), with one also being planned by NIST in the US. There are already dosimetry services using alanine polymer dosemeter dissemination by GSF in Germany, the Istituto Superiore di Sanita (ISS) in Italy, the Japan Atomic Energy Research Institute (JAERI), and the Laboratoire de Metrologie des Rayonnements Ionisants/Commissariat a l'Energie Atomique (LMRI/CEA) of France. A successful ESR alanine radiation measurement intercomparison service, aimed primarily at industrial gamma ray processing plants of member states, was initiated in 1983 by the International Atomic Energy Agency jointly with GSF and is called the IAEA International Dose Assurance Service(56).

ACKNOWLEDGEMENT

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REFERENCES


