
Chapter 1

# Dosimetry of ionising radiation

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## 1.1 - Introduction

Dosimetry of ionising radiation aims to quantify the energy received by a sample of matter (inert matter or living organism) as a result of its interaction with ionising radiation (photons, electrons, protons, neutrons, α particles, etc.). The advantages of EPR in this field are obvious, and its use was first proposed in the 1950s. Indeed, the interaction of Ionising Radiation (IR) with matter generates paramagnetic entities by excitation and ionisation of the atoms, and by breaking the bonds between atoms. These entities, free radicals, defects or ions, can be detected by conventional EPR spectrometry when their lifetime is sufficiently long. As the number of radio-induced paramagnetic species is directly linked to the absorbed dose [1], it can be determined by measuring the intensity of the spectrum. In EPR dosimetry, the absolute number of radio-induced radicals or paramagnetic defects is not measured. Instead, the peak-to-peak amplitude $A_{pp}$

[1] The dose is the energy absorbed per unit of mass of the material being studied. It is expressed in grays [Gy]; 1 Gy = 1 J $kg^{-1}$.



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for a structure of the signal is measured, and the absorbed dose can be deduced by applying one of the following methods:

- One or more calibration curves is created from reference samples with a similar nature to those to be assayed. These samples are irradiated with known doses and the $A_{pp}$ amplitude of their spectrum can be used to establish a curve linking $A_{pp}$ to the dose. When creating the calibration curve, it is important to use a dose range covering all of the doses to be assessed, as extrapolation can be inaccurate due to saturation of the radio-induced signal beyond a certain dose for some materials. The nature of the radiation used to irradiate the reference samples is also very important. Thus, for a given dose, the number of radio-induced species can vary considerably with the type of radiation (photon, electron, neutron, etc.) and the dose rate [in Gy $s^{-1}$]. It is therefore preferable that the characteristics of the calibration beam correspond as closely as possible to those of the radiation to which the samples assayed were exposed. It is not always easy to obtain a source of radiation with the desired characteristics, and it is sometimes necessary to apply correction coefficients. Calibration curves are used with materials presenting little variability, compatible with the desired accuracy of the dose measurement, such as alanine and dental enamel.
- When the sample to be assayed presents broad variability (bone tissues, minerals), the notion of reference sample is no longer valid. In these cases, the "additive dose" method is used, whereby the relationship between $A_{pp}$ and the dose for *the sample under investigation* is established. The sample is irradiated at known doses, to allow its coefficient of sensitivity $\Delta A_{pp}/\Delta\text{dose}$ to be determined, taking matrix effects into account. This coefficient is used to calculate an absorbed dose from the amplitude of the signal recorded before the post-irradiation process.

Since the earliest experiments performed on materials such as glass or alanine [Combrisson and Uebersfeld, 1954; Gordy *et al*., 1955], EPR dosimetry has been used in a wide range of applications:

- dating of archaeological samples based on the accumulated dose of natural irradiation,
- estimation of the dose received by individuals during chronic and/or past exposure, from biopsies of dental enamel,
- estimation of the dose received during recent radiological accidents from biopsies taken from victims or samples of materials worn by them or present in their immediate environment,

- ▹ calibration and control of radioactive sources, generally using alanine as standard,
- ▹ identification of irradiated food products.

This chapter does not aim to be exhaustive, but to use some examples to illustrate the variety of EPR applications in the field of dosimetry of ionising radiation.

## 1.2 - Archaeological dating

### *1.2.1 - Principle of the method*

EPR dating involves quantification of the paramagnetic centres created in a mineral through exposure to *natural radioactivity*. The minerals or biominerals tested are generally embedded in a sediment characterised by a very low level of natural radioactivity, produced by uranium (U), thorium (Th) and potassium (K) contained in some grains. The minerals absorb part of the radiation energy and thus constitute natural dosimeters. The total dose absorbed by the sample throughout its lifetime, known as its palaeodose, is expressed in grays, and can be written:

$$D(T) = \int_0^T d_a(t)\,\mathrm{d}t \qquad [1.1]$$

where $d_a$ is the dose rate (or annual dose) in Gy year$^{-1}$, i.e., the dose absorbed by the sample over a year, and $T$ is the duration of exposure in years, i.e., the age of the sample. When the dose rate is constant, the sample's age is simply given by

$$\text{age} = D(T)/d_a \qquad [1.2]$$

EPR spectrometry can be used to estimate the sample's palaeodose, and the dose rate is calculated from the quantities of radioactive elements (U, Th and its descendents, K) in the sample and the sediment surrounding it.

To be useful in dating, an EPR signal must meet a certain number of conditions: the signal produced by the mineral studied must be radiosensitive; its initial intensity must, if possible, be null; the signal must not be contaminated by other signals; and it must be sufficiently heat-stable to allow dating over a geological timescale. Figure 1.1 shows the EPR spectra produced by the minerals most commonly used in archaeological dating: carbonates of speleothems (stalagmites) and corals, dental enamel and quartz.

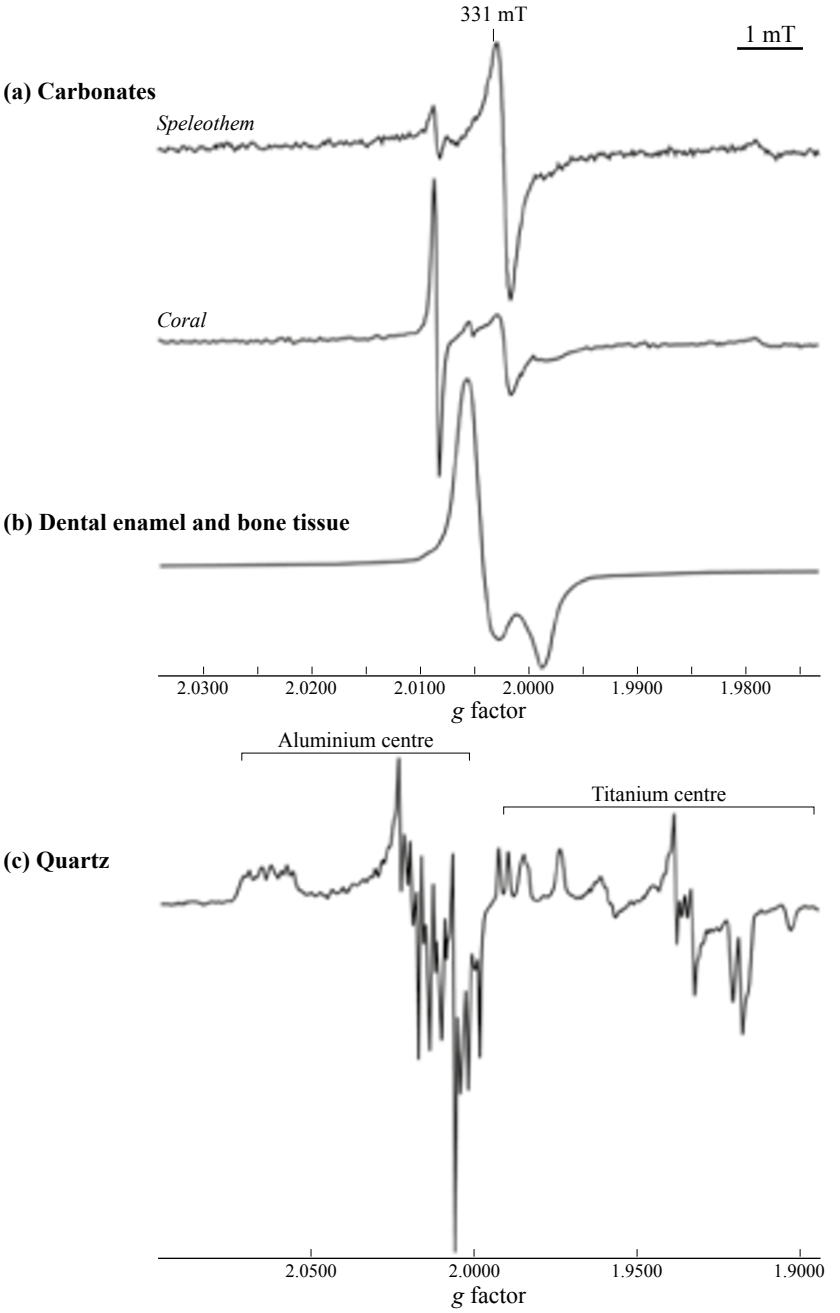


**Figure 1.1** - EPR spectra produced by carbonates (cave calcite, corals), dental enamel and quartz in the $g = 2$ region.

**(a)** Carbonates. Experimental conditions: room temperature, power 5 mW, modulation amplitude 0.1 mT. The carbonate spectra present three radiosensitive lines at $g$ = 2.0057; 2.0036; 2.0007 attributed, respectively, to $SO_2^-$, $SO_3^-$ and $CO_2^-$ radicals associated with a water molecule.

**(b)** Dental enamel and bone tissue. Experimental conditions: room temperature, power 10 mW, modulation amplitude 0.1 mT. The hydroxyapatite signal used in dating is axial with $g_\perp$ = 2.0018; $g_{//}$ = 1.9977. It results from the superposition of several signals attributed to carbonated centres (see section 1.3.1).

**(c)** Quartz. Experimental conditions: $T$ = 100 K, power 5 mW, modulation amplitude 0.1 mT. The *aluminium* centre $[AlO_4]^0$ is characterised by $g$ = 2.0602; 2.0085; 2.0019 and a hyperfine structure due to the Al nucleus ($I$ = 5/2). The *titanium* $[TiO_4]^0$ centres are associated with a compensatory cation ($Li^+$, $Na^+$, $H^+$) and their spectra present a superhyperfine structure due to the cation's nuclear spin (3/2 for $Li^+$ and $Na^+$, 1/2 for $H^+$).

EPR dating can be applied to a wide variety of samples over long time periods. In particular, it can be used to determine chronological reference points for the Lower Pleistocene and the start of the Middle Pleistocene, a period between around 2.0 and 0.5 Ma (figure 1.2).

This method is therefore of great importance, in particular to date samples from the limestone regions of western Europe. For more recent periods, it can be applied in combination with the uranium series (U-Th) method on the same support (dental enamel, mollusc shell, etc.) and the results compared to those obtained by other methods, such as luminescence (thermoluminescence, optically stimulated luminescence) and carbon 14 dating. For recent epochs, the field of application is limited by the radio-sensitivity of the samples.

For more ancient epochs, the number of paramagnetic defects available and their lifetime – if it is too short – are limiting factors which vary depending on the type of sample. Ages of around a million years have been determined from dental enamel and quartz, whereas marine carbonates only appear to be compatible with dating to around a few hundred thousand years.

A summary of the data relating to EPR dating can be found in [Falguères and Bahain, 2002; Grün, 2006]. Application of this method to dating of minerals contained in soils is described in chapter 5 of this volume.

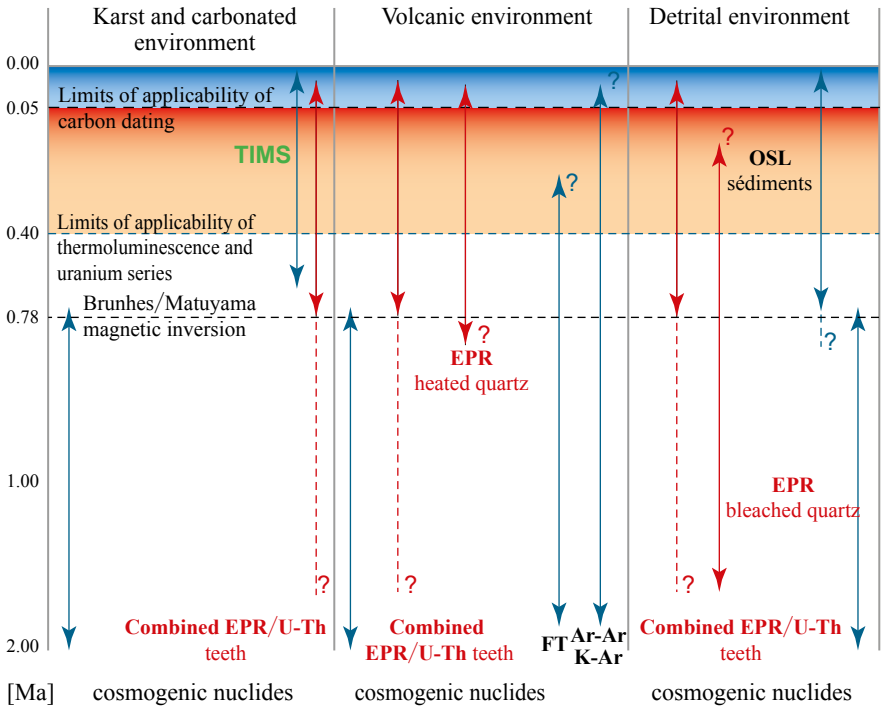


**Figure 1.2** - Comparison of the domains of application of the EPR method and the main methods used to date samples from the Quaternary period, depending on the different types of environment of the prehistoric sites.
**TIMS** = **U-Th** method by thermo-ionisation mass spectrometry;
**FT** = fission track method; **Ar-Ar**/**K-Ar** = argon-argon and potassium-argon methods;
**OSL** = optically stimulated luminescence; **U-Th** = uranium-series method.

### *1.2.2 - Determining the equivalent dose (palaeodose)*

The palaeodose is determined by the additive dose method (section 1.1). Several aliquots of the sample to be dated are artificially irradiated with increasing doses of beta or gamma radiation, and their EPR spectra are recorded. The variation in signal intensity as a function of the dose constitutes the sensitivity curve for the sample, and its extrapolation to an intensity of zero gives the palaeodose (figure 1.3a).

The sensitivity curve is obtained by exposure to a single type of radiation. However, in nature the samples are exposed to complex radiation which includes several types. For this reason, this method does not directly supply the palaeodose, but what is known as an "equivalent dose" $D_E$. The sensitivity curve is generally well described by the following equation:

$$I = I_{\infty}[1 - e^{-\mu(D_{art} + D_E)}] \qquad [1.3]$$

where $I$ is the intensity of the EPR signal of a sample artificially irradiated with the dose $D_{art}$ [Gy], $I_{\infty}$ is the saturation intensity and μ is the sensitivity coefficient [Yokoyama *et al.*, 1985]. Other equations may also be used [Duval *et al.*, 2009].

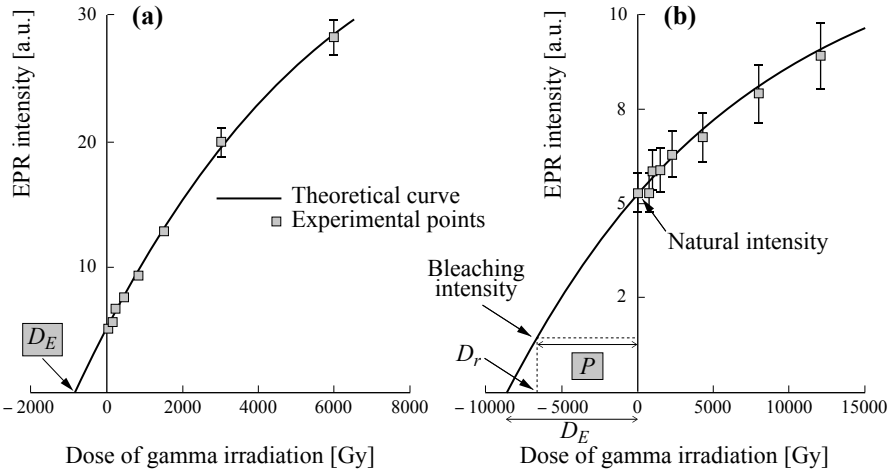


**Figure 1.3** - Sensitivity curves and calculation of the equivalent dose considered as the palaeodose. **(a)** fossilised dental enamel, **(b)** quartz. The dose due to bleaching must be subtracted from the total dose to obtain the archaeological dose. $D_E$ = equivalent dose; $D_r$ = residual dose; $P$ = palaeodose (or archaeological dose) with $D_E = D_r + P$. The continuous line corresponds to calculations performed using equation [1.3].

The quartz grains present in river terraces are often used for archaeological dating. Before sedimenting, these grains were "bleached" by UV radiation from sunlight during their transport by wind and water. This bleaching generates a residual EPR signal which must be subtracted when dating the terrace. To do so, in the laboratory an artificial bleaching experiment is performed on the "natural" aliquot (not artificially irradiated) using lamps which reproduce part of the solar spectrum (figure 1.3b) [Voinchet *et al.*, 2004].

### 1.2.3 - Assessing the dose rate

The annual dose, which is the result of all the ionising radiation to which the sample is exposed over a year, varies depending on the nature of the dose integrator (bone, dental enamel, minerals, sediments). It depends on the concentration and distribution of the radioactive elements in the sample and its environment, and on the intensity of the cosmic radiation. It can be written as follows:

$$d_a = kd_\alpha + d_\beta + d_\gamma + d_{cos} \quad [1.4]$$

where $d_\alpha$, $d_\beta$, $d_\gamma$ and $d_{cos}$ represent the annual doses of α, β, γ and cosmic radiation received by the sample, and $k$ is a factor that takes into account the lower efficacy of α radiation to create trapped electrons. The value of this factor varies depending on the nature of the support. In practice, it is convenient to express the annual dose as a function of the origin of the radiation:

$$d_a = d_{external} + d_{internal} \quad [1.5]$$

The dose due to the radiation external to the sample is measured either *in situ* with the help of a portable gamma spectrometer or a thermoluminescent dosimeter, or in the laboratory on the corresponding sediments. The dose due to the internal radioactivity is *calculated* from the amounts of radioactive elements contained in the sample, as measured by gamma spectrometry in the laboratory. It is rarely constant over time as numerous samples from the quaternary period present radioactive imbalances which must be taken into consideration.

The distribution of uranium in teeth is heterogeneous due to differences in chemical composition of the constituent tissues (enamel, dentine, cement). The uranium content can vary from less than one ppm in well-preserved enamel to more than 100 ppm in altered dentine from the same tooth. When dating fossil dental enamel from samples containing sufficient uranium, the uranium series can be used to calculate variations in annual dose rates. This *post-mortem* enrichment is linked to the difference in solubility between the different valence states of uranium [Gascoyne, 1982]. A number of models have been proposed to describe this phenomenon, such as the early uptake [Bischoff and Rosenbauer, 1981] and linear uptake [Ikeya, 1982] uranium incorporation models.

Grün and collaborators proposed combining U-Th and EPR data when calculating the age $T$ of fossil samples. They described how the samples' uranium content changes over time by using the $U(t)$ function below [Grün *et al.*, 1988]:

$$U(t) = U_0 (t/T)^{p+1} \quad [1.6]$$

*where* $U_0$ is the uranium content measured, and $p$ is the diffusion parameter for uranium, determined simultaneously from the EPR and U-Th data. The function $U(t)$ is illustrated in figure 1.4 for a few values of $p$.

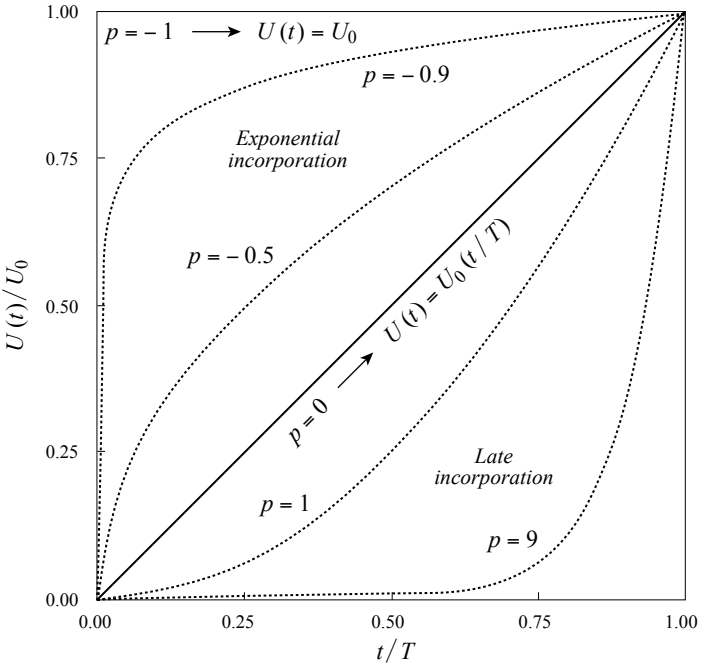


**Figure 1.4** - Curves describing the incorporation of uranium over long time periods, as calculated using equation [1.6]. [From Grün *et al.*, 1988]

## 1.2.4 - Examples of archaeological and geological dating

### ◇ *Visogliano paleolithic site, Italy*

Among the sites in western Europe, the Visogliano deposit, located in the karst around Trieste, Italy, is considered by pre-historians as a reference sequence for the Middle Pleistocene, the period between –780,000 and –130,000 years. This deposit contained fossil human remains, attributed to *Homo heidelbergensis*, prehistoric tools and animal bones [Abbazzi *et al.*, 2000]. This site contains a large number of well-defined successive archaeological layers from which it was possible to establish a chronostratigraphy so as to situate this sequence in a broader context at the level of western Europe. Teeth from large herbivores from the deposit were dated by the combined EPR/U-Th method [Falguères *et al.*, 2008]. The oldest layers were dated at between –480,000 and –360,000 years (figure 1.5). As these lower levels contained most of the human remains, the results give a minimum age of –350,000 years for Visogliano Man.

### ◇ *Fossil river formations of the Creuse valley, France*

When the bones and teeth are altered or absent from a site, quartz is often the only support which can be dated by EPR in a non-volcanic environment [Falguères and Bahain, 2002]. This was the case, for example, in the Creuse valley, which presents a system of alluvial terraces covering the whole Quaternary period, i.e., around the last two-million years (figure 1.6) [Despriée *et al*., 2006]. Numerous samples were collected from the different terraces and the ages determined by EPR were used to propose, for the first time, an interesting and solid chronological frame for this region. Several prehistoric sites were discovered in the fluvial formations in this valley. One of the most ancient deposits was found at Pont-de-Lavaud, an open-air site consisting of deposits on a riverbank. It is fossilised in a very high fluvial terrace located more than 100 m above the current level of the Creuse, and was dated at around 1 million years.

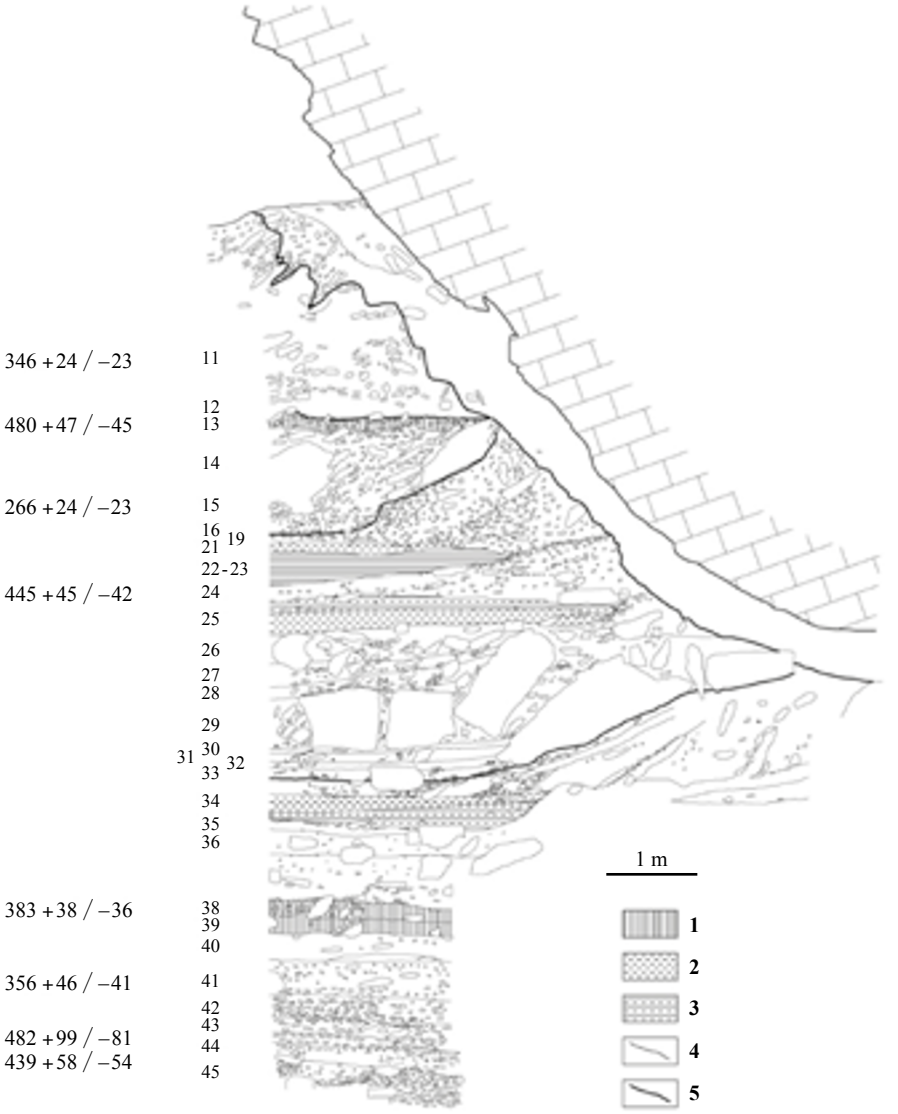


**Figure 1.5** - Longitudinal profile of the Visogliano site showing how the main geoarcheological levels, numbered from 11 to 45 are arranged.The ages determined by the EPR/U-Th method are expressed in ka on the left. **1**: occupied soils, **2**: læss levels, **3**: altered læss levels,**4**: limits of lithological units, **5**: main discontinuities.

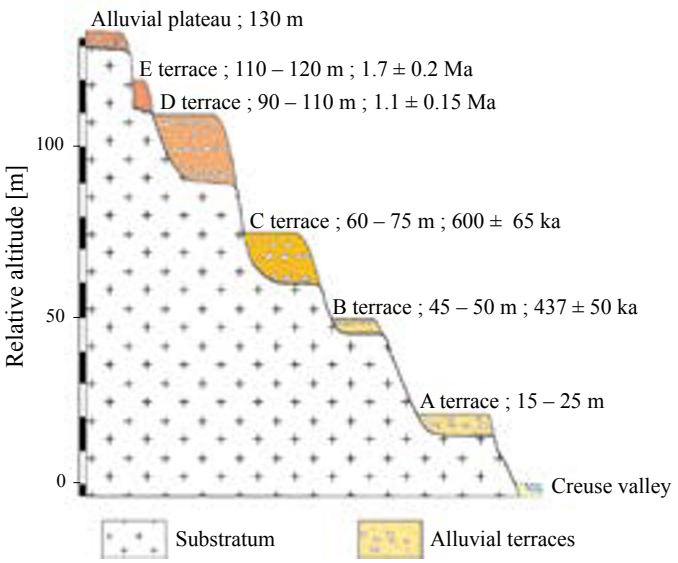


**Figure 1.6** - EPR dating of various fluvial terraces in the Creuse valley, France. The results cover almost the whole Quaternary period, i.e., around 2 million years.

## 1.3 - Retrospective dosimetry and radiation accident dosimetry

In this context, the aim of the study is to make a *post hoc* estimation of the doses of Ionising Radiation (IR) received by individuals in case of accident or chronic external exposure [2]. In the case of past and/or chronic exposure, it is mainly a question of comparing the estimated doses and the effects observed (cancer and non-cancer, cataract, fibrosis, infarct, etc.) to better understand the effects of IR on health in the context of epidemiological or radiobiological studies. With recent acute accidental irradiation, it is a question of helping to diagnose victims to allow healthcare teams to determine the most appropriate therapeutic strategy or to identify people who were exposed during a major accident.

EPR spectroscopy is one of the techniques used in retrospective dosimetry. Indeed, as the circumstances of the exposure are very varied and generally poorly known, a single technique cannot always reliably estimate the received dose. It is therefore often necessary to apply a multi-technique approach (cytogenetics, luminescence, numerical simulation) to better determine the received doses [Alexander *et al*.,

[2] The source of radiation is outside the organism, unlike with 'internal' exposure, which is induced by inhalation or ingestion of radioactive products.

2007; Simon *et al*., 2007; Trompier *et al*., 2010; Ainsbury *et al.,* 2011]. In the case of severe irradiation, the dose is generally very heterogeneously deposited and the EPR approach can be used to determine its distribution in the organism.

### 1.3.1 - Chronic and/or past exposure

During chronic exposure, individuals are exposed to relatively low doses, but on a permanent or semi-permanent basis over relatively long periods, from a few months to several decades. It could be the result of exposure to "reinforced" natural radiation due to radon [3] or exposure linked to radioactive contamination of the environment (Chernobyl, Mayak, radium industry [4]) or of contaminated materials used to build housing, as was the case in Taiwan [5]. Assessing the received dose during past exposure can improve what we know about the long-term effects of IR. Thus, the whole modern radioprotection system, for example the definition of the statutory exposure limits, is based in large part on the effects observed on survivors of the Nagasaki and Hiroshima bombings. Retrospective dosimetry techniques have, in particular, been used to estimate the doses received during these two explosions.

Although in some cases the main parameters of the exposure can be assessed, and the dose estimated by applying models to this data, it is always preferable to validate these approaches through direct measurements of the dose received by exposed persons or by materials contained in their environment or on the site of the accident. EPR spectra for biopsies of dental enamel is a reference method in this field. Like bone tissue, dental enamel is mainly composed of hydroxyapatite crystals $(Ca)_{10}(PO_4)_6(OH)_2$ (96 % of the mass), but it is better crystallised and contains much less water (3 %) and organic matter (1 %). It has numerous advantages over bone from the point of view of measuring the dose by EPR:

- the signal induced by irradiation is specific for the interaction with the IR,
- some components of the radio-induced signal are extremely stable over time (half-life around $10^7$ years), which is rare,

[3] Radon is a rare gas produced by thorium 232 and uranium 238 decay, it is naturally present in the earth's crust, mainly in granitic rocks. Its isotopes are radioactive.

[4] After the discovery of radium by Marie Curie, an industry was developed to produce radium from uranium ore for a range of applications: luminescent paints, cosmetics, energy drinks, etc. Some sites where this activity was performed remain contaminated to this day.

[5] Iron contaminated with cobalt 60, a radioactive element, was used in the construction of housing in Taiwan. It resulted in chronic exposure of the residents over several years.

- paramagnetic species are extensively produced, which makes it possible to detect relatively low doses. The limit of detection is around 50 mGy for 100 mg, whereas the annual dose received by the enamel in normal conditions is around a few mGy,
- the variation in signal intensity as a function of the dose can be considered linear and the inter-sample variability is relatively weak (standard deviation around 10 %), which makes it possible to use pre-established calibration curves.

Most radio-induced species are either carbonate groups ($CO_2^{\bullet -}$, $CO_3^{\bullet -}$, $CO^{\bullet -}$, $CO_3^{\bullet 3-}$, etc.), phosphate groups ($PO_4^{\bullet 2-}$), or oxygen derivatives ($O_3^{\bullet -}$, $O^{\bullet -}$, etc.). But not all are heat-stable. For example, the $CO_3^{\bullet -}$ radical disappears at room temperature a few weeks after irradiation. Figure 1.7 shows the EPR spectrum for a sample of dental enamel which received a dose of 500 mGy and the simulation obtained by superposing the radio-induced signal on the "native" signal (present before irradiation).

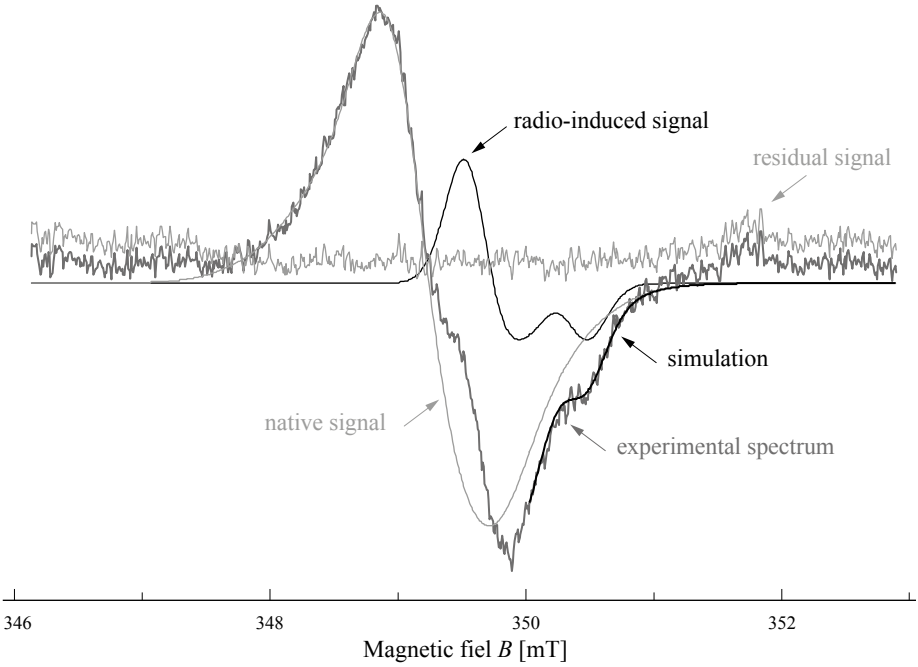


**Figure 1.7** - X-band spectrum for a sample of dental enamel irradiated at 500 mGy. Experimental conditions: room temperature, microwave power 2 mW. The simulation shows that it results from the superposition of a radio-induced component and a "native" component. The "residual signal" is the difference between the experimental spectrum and the simulation.

Numerous studies have been performed to identify the various components of the radio-induced signal and the associated paramagnetic species [Fattibene and Callens, 2010]. At X-band, the spectrum has the appearance of an axial signal characterised by $g_{//} = 2.0018$ and $g_{\perp} = 1.9971$, but in reality it includes a dominant rhombic component and an axial component. Today, it is relatively well established that these two components are due to $CO_2^{\bullet -}$ radicals located in two different environments [Vanhaelewyn *et al.*, 2002]. The "native" signal present before irradiation, characterised by $g = 2.0045$ and a peak-to-peak width $\Delta B = 0.8$ mT, is due to organic matter present in the enamel. It disappears when this matter is eliminated. The various components of this signal and the associated paramagnetic species have not yet been clearly identified.

The two methods described in section 1.1 can be used to estimate the dose received by the dental enamel. The additive dose method is generally considered more accurate [Wieser *et al.*, 2005]. However, it involves destruction of the initial information and it is time-consuming to perform as well as requiring ready access to irradiation devices. It is thus more appropriate to use a pre-established calibration curve when studying a large number of samples. The advantages and disadvantages of the two methods are discussed in [IAEA, 2002] and [Fattibene and Callens, 2010].

Several parasitic effects can introduce bias when determining the intensity of the radio-induced signal and the associated dose. For example, drilling the teeth induces a heat-stable "mechanical" signal, characterised by $g = 2.002$ and $\Delta B = 0.8$ mT (figure 1.8).

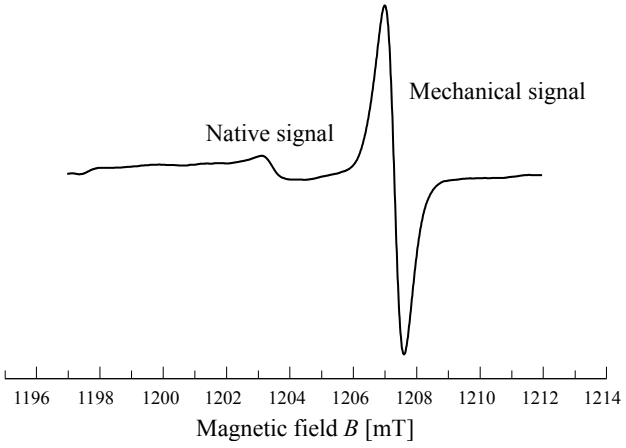


**Figure 1.8** - Q-band EPR spectrum for a sample of mechanically-stressed calcified tissue. Experimental conditions: room temperature, power 1 mW.

This signal is due to radicals formed by the mechanical stress, mainly located at the surface of samples. It can be subtracted from the spectrum by simulation or suppressed by treating the sample with dilute acetic acid to uniformly eliminate the surface layer of the enamel. UV radiation and irradiation produce identical radicals, which can lead to overestimation of the received dose [Romanyukha *et al.*, 1996]. To avoid this potential pitfall, samples from the front faces of the canines and incisors are generally not used.

In contaminated areas, doses linked to the ingestion or inhalation of radioactive particles are added to the external irradiation. In some cases, radioactive contaminants can significantly increase the dose deposited in dental enamel, and as a result the dose estimated in the enamel will no longer be the external dose due to emissions from radioactive deposits in the environment. This is the case of strontium 90, a beta emitter, with chemical properties similar to those of calcium, which preferentially binds to dental enamel or dentine (the internal part of the tooth) as the teeth grow. Strontium generates localised dose deposits due to the short trajectory of beta radiation in these tissues. These localised deposits can result in significant local doses. As a result, the doses measured in the enamel must be interpreted carefully and additional measurements and calculations are often required [Simon *et al.,* 2007]. This type of contamination occurred, for example, in the Techa river basin in Russia.

Most applications of dosing using dental enamel relate to exposure to photonic radiation. In the case of victims of the Hiroshima and Nagasaki bombings, a neutronic component must be added [Ikeya, 1993]. The characteristics of the radio-induced signals are identical in both cases, but at equal dose, the intensity of the EPR signal induced by neutrons only represents a few % of that of the signal induced by photons [Trompier *et al*., 2006].

In conclusion, using EPR to measure the dose in samples of dental enamel is recognised as a valid technique to estimate received doses linked to external exposure, whether recent or past, high or low. Nevertheless, there remain a certain number of open or unresolved questions (influence of UV, origin of signals), the resolution of which could ultimately improve the performance of this method. A very detailed literature review on this topic, covering the last 30 years, can be found in [Fattibene and Callens, 2010].

### 1.3.2 - Radiation accident dosimetry and emergency situations

Radiological accidents [6] result in a wide range of situations as they can involve a variety of types of radiation (photon, electron, neutron, etc.), energies (from a few meV to a hundred MeV) and accidental circumstances (duration, topology, number of victims). Such accidents can occur in industrial installations, during manipulation of sources or particle generators, in a nuclear setting (e.g. criticality accidents), during the recovery or theft of "orphan sources" [7], malicious use of radioactive substances, or in a medical context, mainly during radiotherapy and interventional radiology. These accidents sometimes lead to extreme exposure, and can have a significant impact on victims' health, occasionally requiring amputations and even causing death. It is therefore important to diagnose exposure as precisely as possible to better adapt the treatment offered to victims of irradiation. Several techniques can be implemented to estimate effects on the body as a whole, otherwise, the distribution of the dose can be determined for the whole body or for specific organs of interest, such as haematopoietic centres [8] and the skin. In complement to the analysis of clinical symptoms (vomiting, rash, necrosis, aplasia), accident reconstruction techniques or biological or physical retrospective dosimetry are used. There is no "standard" or ideal method. These techniques are often complementary and that selected will depend on the type of accident (localised or whole-body irradiation), the type of radiation involved, the time since irradiation, access to the site of the accident and/or to patients for biopsy biodosimetry, and information on the circumstances and parameters of the accident.

Estimation of the received dose by EPR has the advantage of not requiring information on the circumstances of the accident [9], which is generally partial and imprecise. Another advantage is that it can estimate the received dose at several points in the victims' bodies, as most irradiation is very heterogeneous or localised and produces very strong dose gradients. In this case, the mean whole-body dose, estimated on blood samples by cytogenetic techniques, provides no information on the damage incurred locally by the body.

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6 Here, we only mention accidents linked to external exposure as approaches to estimate exposure following ingestion or inhalation have yet to be described.

7 Orphan sources are radioactive sources which have been abandoned or left unattended, and sometimes without any particular identification.

8 Red bone marrow, responsible for the production of blood cells.

9 Unlike accident reconstruction techniques, whether experimental or digital.

Materials eligible for this EPR dosing must present an exploitable EPR signal, if possible characteristic and measurable several weeks or several months after the accident, from dose-levels greater than around a few Gy. Although the potentially lethal whole-body dose is around 4 to 6 Gy, doses of up to several thousand Gy involving small volumes with very heterogeneous irradiation may not endanger the victims' lives in the short-term [Huet *et al*., 2007]. Numerous materials are likely to present the required properties, but they must be present during the irradiation and recoverable for analysis. In the case of accidents for which dosimetric analyses have been published, *calcified tissues* (dental enamel and bone) were the main samples used [Trompier *et al*., 2007; Clairand *et al.*, 2006]. These materials present good sensitivity to IR and give a stable EPR signal. Although the sensitivity of bone tissues is 10- to 20-fold lower than that of dental enamel, it remains sufficient to perform measurements, particularly when biopsies of bone tissue (generally a few mg) are taken near to the most irradiated zones, where the doses are high. The distribution of the bone tissues throughout the body means that samples can be obtained whatever the configuration of the irradiation and the location of the dose deposit. The dosimetric signal given by bone tissues has the same characteristics as that of dental enamel. However, the bone is living material which completely renews itself every 7–8 years, as a result the signal decreases over time. Nevertheless, once extracted, the signal is as stable as that for dental enamel. In radiation accident dosimetry, where the dose must be measured very precisely, the additive dose method is preferred due to the significant variability in dose-sensitivity observed with bone tissues.

To limit the invasiveness of the sampling, measurements can be performed *in vivo* on exposed teeth or bone tissues located near to the surface [Swartz *et al*., 2006; Zdravkova *et al*., 2004]; alternatively, micro biopsies (1–2 mg) can be used, taking advantage of the greater sensitivity of EPR at higher frequencies (K- and Q-bands) [Romanuykha *et al.,* 2007; Gomez *et al*., 2011; Trompier *et al*., 2010]. To perform *in vivo* measurements, surface antennae and a low-frequency (0.3 to 2 GHz) spectrometer are used, making it possible to study dense samples which may contain a significant proportion of water without causing heating of the tissues. Sensitivity with this technique is lower than at X-band, with a limit of detection of around 1 to 2 Gy for *in vivo* measurements at L-band on molars or pre-molars, whereas it is around 0.5 Gy at Q-band with 2–3 mg of enamel. These two techniques have yet to be used in real cases of accidents.

They appear promising, but numerous technical and methodological obstacles remain to be overcome.

Other materials present on the victims or in their environment can be used in EPR dosimetry. For example, sucrose can be used [Nakajima, 1994; Hütt *et al*., 1996; Kai *et al*., 1990; Shirashi *et al.*, 2002] as can soda-lime glass from watches [Wu *et al*., 1998]. Figure 1.9 shows the EPR spectra for irradiated sucrose and soda-lime glass samples, the latter was taken from a liquid-crystal screen from a mobile telephone [Trompier *et al*., 2011].

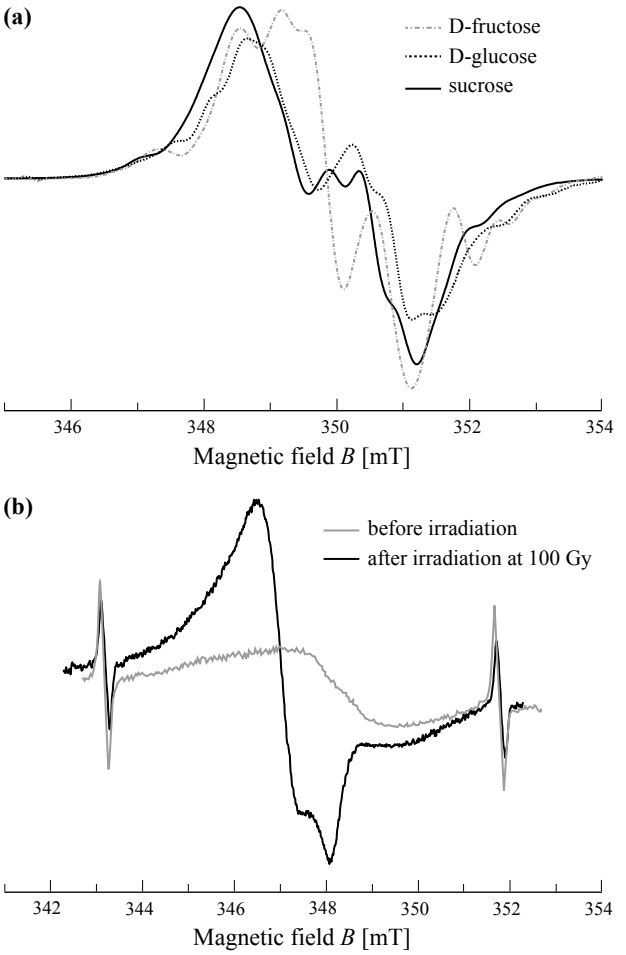


**Figure 1.9** - X-band EPR spectra for various irradiated samples. **(a)** Samples of sucrose and the two monosaccharides composing it were irradiated at 100 Gy and their spectra were recorded. **(b)** Soda-lime glass, before and after irradiation at 100 Gy. Spectra were recorded at room temperature at 2 mW.

A recent study identified up to six radio-induced radicals in sucrose [De Cooman *et al*., 2008]. In the case of soda-lime glass, photons produce a signal which is generally attributed to $O^{\bullet -}$ ions, but neutrons, α particles and photons at very high doses (greater than a kGy) produce $E'(O \equiv Si^{\bullet})$ centres [Ikeya, 1993]. Sugars in general and some food additives (sorbitol, ascorbic acid, aspartame, etc.) can be used in EPR dosimetry [Hervé *et al.*, 2006]. Other potentially informative materials (polymers, cotton, wool, leather, table salt, nail fragments, hair clippings, etc.) have never been used in practice, either because they are not widely available, or because of unstable signals, or indeed because the relevant methods have yet to be validated. A complete description can be found in [Trompier *et al.* 2009a].

Among all these materials, nail fragments are by far the most interesting, particularly in cases of irradiation of the hands or feet, which is common during accidents. However, the method to estimate the received dose has not yet been established as the radio-induced signal is difficult to distinguish from signals induced by mechanical stress [Trompier *et al*., 2009b].

In conclusion, EPR is frequently used to estimate the doses received during accidental exposure. The most frequently used materials are calcified tissues, sugars and glass. Other materials are regularly reviewed and particular efforts are being made to develop methods for use with common materials (glass from liquid-crystal screens and polymers from plastic cases, keyboards and screens from mobile phone), to allow EPR dosimetry to be used as a method to sort populations when major accidents occur.

## 1.4 - A reference method: Alanine/EPR dosimetry

In metrology for ionising radiation, several techniques are used to measure the absorbed dose: calorimetry, ionometry, thermoluminescence, chemical dosimetry. EPR dosimetry of alanine is one of these reference techniques.

### *1.4.1- Description of the method*

Alanine is an amino acid of formula $H_2N–CH(CH_3)–COOH$. L–α–alanine in a polycrystalline state is used in dosimetry. Samples are conditioned as powders, films or pellets (figure 1.10).

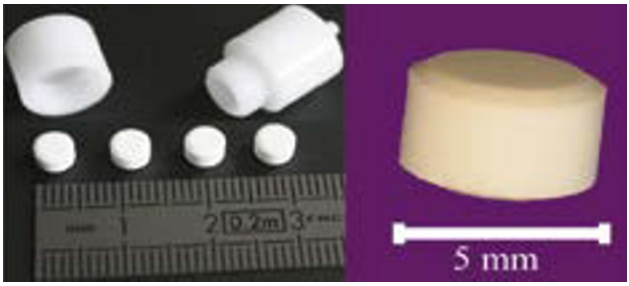


**Figure 1.10** - Alanine dosimeter containing several pellets and its container.

Radiolysis of polycrystalline alanine is a complex process which leads to the formation of several stable free radicals which generate the EPR spectrum presented in figure 1.11.

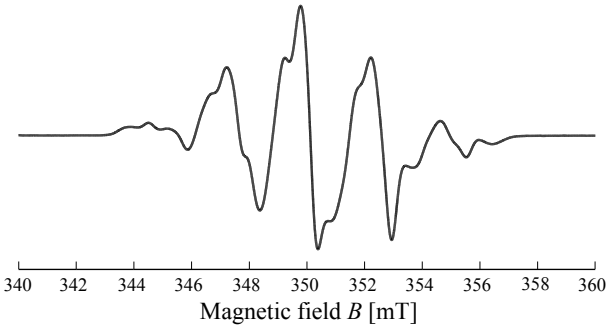


**Figure 1.11** - X-band EPR spectrum obtained by radiolysis of alanine in the solid phase (powder). Experimental conditions: power: 2 mW, modulation: frequency 100 kHz,amplitude 0.3 mT.

This spectrum was simulated by superposing two major components attributed to the $H_3C–^{\bullet}CH–COOH$ (55 %) and $H_3C–^{\bullet}C(NH_3^+)–COO^-$ (35 %) radicals and a less-well-defined minor component [Hydari *et al.*, 2002; Malinen *et al.*, 2003]. However, it should be noted that spin trapping experiments (see chapter 3 in this volume) of radicals created by radiolysis of polycrystalline alanine only detected two species, in different proportions to those indicated above [Raffi *et al.*, 2008].

In dosimetry, the amplitude of the central peak on the spectrum is measured. The relation between this amplitude and the dose received by the sample depends on numerous factors that can be classified in two categories [Dolo *et al.*, 1998; Dolo *et al.*, 2005]:

- The first relates to the parameters influencing the physico-chemical reaction and the environmental conditions in which it takes place:
  - the dose rate and the duration of irradiation,
  - the temperature and relative humidity,
  - the rate of recombination of the radical species created.
- The second relates to the conditions in which the EPR spectrum is recorded, i.e., the acquisition parameters per se (power, modulation amplitude, etc.) but also the temperature and relative humidity in the cavity and, naturally, the mass of the sample.

In dose metrology, all these parameters are precisely defined. In particular, dosimeters must be designed to avoid radical mobility and water absorption. The quantitative control of the EPR spectrum for alanine has made it a reference method for the dosimetry of high doses ($10^2$ to $10^5$ Gy) [Regulla *et al.*, 1982] but also for lower doses, such as those used in radiotherapy (2 to 50 Gy) [Garcia *et al.*, 2009]. It can be used to measure doses with an uncertainty of less than around 2 %.

### 1.4.2 - Research and development in radiotherapy

For a number of years, research into alanine-EPR dosimetry has focused on increasing the sensitivity of the method for the range of doses used in radiotherapy (2–50 Gy). Several axes of development are currently under investigation in metrology laboratories, in particular to improve the detector, the acquisition parameters and exploitation of EPR spectra [Garcia *et al.*, 2009].

Every year, around 200,000 patients in France and 1 million in Europe are treated by radiotherapy, whatever the technique. The new systems which emerged over the last few years use several beams of small dimension, the orientation of which varies during each treatment session. This is the case, for example with tomotherapy-type systems Cyberknife®, arctherapy and Gamma-Knife. As the irradiation conditions are very different to those defined in the reference radiotherapy protocols, specific metrological adaptations must be made. Alanine dosimeters can be very useful in this field thanks to their small size and their specificities (non-destructive measurements, integrating dosimeter affected neither by the dose rate nor by the energy) which make their use very flexible. They can thus be used to calibrate beams or to verify the dose delivered by irradiating the dosimeters in the conditions used to treat patients.

When using photons, the reference conditions for accelerator calibration are a $10 \times 10$ cm$^2$ irradiation area, with the dosimeter placed in a vat of water measuring $30 \times 30 \times 30$ cm$^3$ at 10 cm depth and at a distance of 1 m from the source of radiation. During a tomotherapy session, the source of radiation moves around the patient in a ring. The ring has a radius of 85 cm and the surface area has a maximal field of $40 \times 5$ cm$^2$. In this case, the reference protocol cannot be used. To calibrate this type of radiation source by alanine EPR, a series of dosimeters must first be irradiated in the reference conditions using a beam with a known dose rate. This first step can be used to establish a calibration curve, which gives the intensity of the EPR signal as a function of the dose. This curve is linear over the range of doses used in radiotherapy (figure 1.12).

Dosimeters are then placed on the tomotherapy apparatus, irradiated and analysed by EPR, and the received dose is deduced from the reference curve by applying corrections linked to the geometry of the irradiation device. In this case, it is essential to consider the area of the field, the source-detector distance, the depth in water. For the area of the field, numerical simulations are required. For the source-detector distance and the depth in water, the correction simply involves the $1/d^2$ variation and the value of the absorption coefficients, respectively [Perichon *et al.*, 2011].

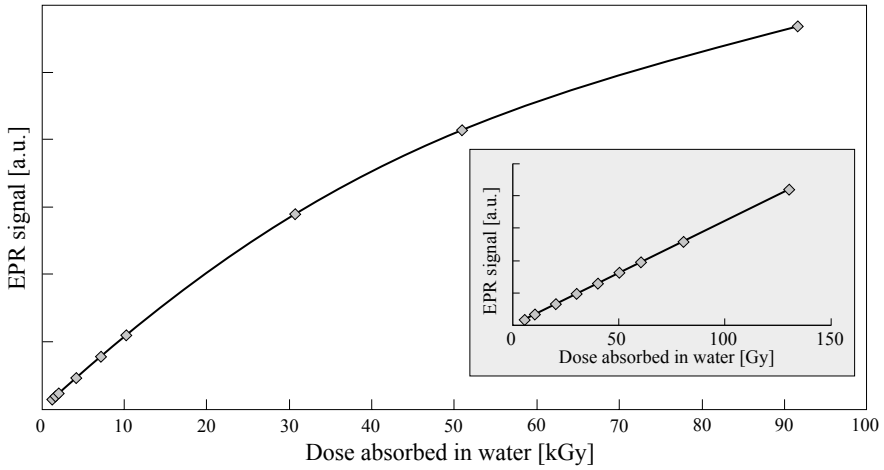


**Figure 1.12** - Examples of alanine calibration curves for various dose ranges.

Electron beam radiotherapy is used to treat tumours at a low depth. In this case, EPR alanine dosimetry can also be used, on the condition that a calibration curve is established using an electron beam. Indeed, for the same irradiation dose

in water, the EPR signal produced by an electron beam is somewhat weaker than that produced by a photon beam. The calibration curve is linear over the 8–22 MeV energy range used in radiotherapy.

Proton therapy is used to treat tumours located close to very sensitive organs, particularly in the head. Indeed, proton beams can destroy cancerous cells at a well-defined depth within the body without affecting neighbouring healthy cells. Alanine EPR dosimetry can also be used with this technique, but few studies have been devoted to this subject.

### 1.4.3 - Sterilisation by irradiation

Alanine EPR dosimetry is a reference technique for industrial irradiation [ISO/ASTM 51607, 2004]. Irradiation is used for sterilisation, to improve hygiene and to increase the shelf-life of a range of food and health products [IAEA, 1999]. This procedure generates low heat and provides better sterilisation than traditional techniques, some of which have been shown to be dangerous to consumers, such as fumigation with ethylene oxide. Irradiation is used in numerous activity sectors, and is associated with strict regulatory controls:

- medicine: sterilisation of single-use materials (syringes, catheters, prostheses), food for immunodepressed patients, or blood products,
- pharmacy: sterilisation of some innovative biotechnological and/or thermosensitive drugs, in particular amino-acid-based treatments,
- food and agriculture: disinfection of foods contaminated due to human manipulation (e.g. mechanically separated meats) or deinfestation of naturally contaminated substances (e.g. spices).

In all these sectors, the statutory authorisations indicate characteristic product-by-product dose levels aiming to guarantee a degree of sterility varying from the maximum level (sterility in the medical sense of the term) to simple "hygienic" measures. As these doses are in the range of a few tens of grays to several kilograys, alanine EPR dosimetry is particularly well adapted to their measurement.

## 1.5 - Identifying irradiated food products

The quality of irradiated food products is guaranteed by the requirements to ensure traceability of the received doses and labelling. The term retained for

the use of this procedure is *ionisation*, and in Europe a logo must be displayed on any ionised product, even if only some of the ingredients were ionised (figure 1.13).

**Figure 1.13 -** Logo which must be present on all ionised food products.

In this context, the legislation has two main objectives. A standard authorises the treatment of food products by ionisation with, for each authorised product, an indication of the doses to be applied. Another standard authorises the ionised products and their circulation, with an obligation of clear labelling for consumer's information. These statutory obligations have been associated with control methods to combat fraud [Raffi, 2003]. The first objective is to detect irradiated foods first by applying a qualitative approach, then a quantitative approach which aims to assess whether the doses delivered conformed to the prescriptions. Several European standards have defined protocols for use with a range of products. EPR was recognised as appropriate for these requirements and it is used to this end for:

- meat and fish bones, by measuring radicals of hydroxyapatite,
- strawberries, pistachios and paprika, measuring the characteristic signal produced by cellulose,
- dried fruits (figs, papaya, raisins), measuring the signal from semiquinone radicals produced from crystallised sugars.

These protocols are reliable enough to simply and rapidly guarantee proof that the conditions of application were in line with the statutory prescriptions. They are often extended to other products, but only as part of routine verifications to detect unexpected product behaviour.

## 1.6 - Conclusion

Measuring the dose of ionising radiation absorbed by matter based on EPR quantification of paramagnetic species is used in a wide range of fields: archaeological dating, study of the effects of radiation on the body, management of radiological accidents, metrology, detection of irradiated food products. This variety of applications is possible thanks to the sensitivity of EPR, the wide range of exploitable signals and the ease with which their amplitude can be measured. *Alanine*/EPR dosimetry can be used to estimate doses over a very broad range, from a few tens of mGy to the MGy, it is non-destructive and can be applied to a wide range of materials. It thus offers many possibilities in dosimetry and recent technical developments in instrumentation should increase its use in this field.

## References


Abbazzi L. *et al.* (2000) *Journal of Archaeological Science* **27**: 1173-1186.

Ainsbury E.A. *et al.* (2011) *Radiation Protection Dosimetry* **147**: 573-592.

Alexander G.A. *et al.* (2007) *Radiation Measurements* **42**: 972-996.

Bischoff J.L. & Rosenbauer R.J. (1981) *Science* **213**: 1003-1005.

Clairand I. *et al.* (2006) *Radiation Protection Dosimetry* **120**: 500-505.

Combrisson J. & Uebersfeld J. (1954) *Comptes Rendus Hebdomadaires de l'Académie des Sciences* **238**: 572-574.

De Cooman H. *et al.* (2008) *Journal of Physical Chemistry B* **112**: 7298-7307.

Despriée J. *et al*. (2006) *Comptes Rendus Palevol* **5**: 821-828.

Dolo J.-M., Raffi J. & Piccerelle P. (2005) *Revue Française de Métrologie* **4**: 5-15.

Dolo J.-M., Pichot E. & Feaugas V. (1998) *Applied Magnetic Resonance* **15**: 269-277.

Dolo J.-M. & Feaugas V. (2005) *Applied Radiation and Isotopes* **62**: 273-280.

Duval M. *et al.* (2009) *Radiation Measurements* **44**: 477-482.

Falguères C. & Bahain J.J. (2002) « La datation par résonance paramagnétique électronique (RPE) » *in Géologie de la Préhistoire, Méthodes, Techniques, Applications* Miskovsky, J.-C., ed., Géopré.

Falguères C. *et al*. (2008) *Quaternary Geochronology* **3**: 390-398.

Fattibene P. & Callens F. (2010) *Applied Radiation and Isotopes* **68**: 2033-2116.

Garcia T. *et al.* (2009) *Radiation Physics and Chemistry* **78**: 782-790.

Gascoyne M. (1982) « Geochemistry of the actinides and their daughters » in *Uranium series disequilibrium: applications to environmental problems*, Ivanovich M. and Harmon R.S. eds, Oxford University Press.

Gómez J.A. *et al.* (2011) *Radiation Measurements* **46**: 754-759.

Gordy W., Ard W. & Shields H. (1955) *Proceedings of the National Academy of Sciences of the USA* **41**: 983-996.

Grün R., Schwarcz H.P. & Chadam J. (1988) *Nuclear Tracks* **14**: 237-241.

Grün R. (2006) *Yearbook of Physical Anthropology* **49**: 2-48.

Herve ML. *et al.* (2006) *Radiation Protection Dosimetry* **120**: 205-209.

Huet C. *et al.* (2007) *Radioprotection* **42**: 489-500.

Hütt G., Brodski L. & Polyakov V. (1996) *Applied Radiation and Isotopes* **47**: 1329-1334.

Hydari M. *et al*. (2002) *Journal of Physical Chemistry A* **106**: 8971-8977.

IAEA (International Atomic Energy Agency) (1999) Proceedings of the IAEA International Symposium on Techniques for High Dose Dosimetry in Industry, Agriculture and Medecine, IAEA TECDOC 1070, Vienna.

IAEA (International Atomic Energy Agency) (2002) IAEA TECDOC 1331, Vienna.

Ikeya M. (1982) *Japanese Journal of Applied Physics* **22**: 763-765.

Ikeya M. (1993) *New Applications of Electron Spin Resonance-Dating, Dosimetry and Microscopy*. World Scientific, Singapore.

ISO/ASTM (2004) n°51607.

Kai A., Ikeya M. & Miki T. (1990) *Radiation Protection Dosimetry* **34**: 307-310.

Malinen E. *et al.* (2003) *Radiation Research* **159**: 23-32.

Nakajima T. (1994) *Applied Radiation and Isotopes* **45**: 113-120.

Périchon N. *et al.* (2011) *Medical Physics* **38**: 1168-1177.

Raffi J. *et al.* (2008) *Spectrochimica Acta Part A*, **69**: 904-910.

Raffi J. (2003) *Techniques de l'ingénieur*, IN 12.

Regulla D.F. & Deffner U. (1982) *International Journal of Applied Radiation and Isotopes* **33**: 1101-1114.

Romanyukha A.A., Wieser A. & Regulla D.F. (1996) *Radiation Protection Dosimetry* **65**: 389-392.

Romanyukha A. *et al.* (2007) *Health Physics* **93**: 631-635.

Shiraishi K. *et al.* (2002) *Advances in ESR Applications* **18**: 207-209.

Simon S.L. *et al.* (2007) *Radiation Measurements* **42**: 948-971.

Swartz H.M. *et al.* (2006) *Radiation Protection Dosimetry* **120**: 163-170.

Trompier F. *et al.* (2006) *Radiation Protection Dosimetry* **120**: 191-196.

Trompier F. *et al.* (2007) *Radiation Measurements* **42**: 1025-1028.

Trompier F. *et al.* (2009) (a) *Annal of Istuto Superiore di Sanità* **45**: 287-296.

Trompier F. *et al.* (2009) (b) *Radiation Measurements* **44**: 6-10.

Trompier F. *et al.* (2010) *Radiation Protection Dosimetry* **144**: 571-574.

Trompier F. *et al.* (2011) *Radiation Measurements* **46**: 827-831.

Vanhaelewyn, G.C.A.M. *et al.* (2002) *Radiation Research* **158**: 615-625.

Voinchet P. *et al.* (2004) *Quaternaire* **15**: 135-141.

Yokoyama Y., Falguères C. & Quaegebeur J.P. (1985) *Nuclear Tracks* **10**: 921-928.

Wieser A. *et al.* (2005) *Applied Radiation and Isotopes* **62**: 163-171.

Wu K. *et al.* (1998) *Radiation Protection Dosimetry* **77**: 65-67.

Zdravkova M. *et al.* (2004) *Physics in Medicine and Biology* **49**: 2891-2898.