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A POINT OF VIEW ABOUT IDENTIFICATION OF IRRADIATED FOODS BY
ELECTRON SPIN RESONANCE

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BY ELECTRON SPIN RESONANCE

Louis SAINT-LEBE and Jacques RAFFI

Principles and conditions required for using electron spin resonance (ESR) in identifying irradiated foods are first put forth. After a literature review, examples of irradiated cereals and French prunes are described in order to derive general conclusions concerning the futur of ESR in this field.

UTILISATION DE LA RESONANCE PARAMAGNETIQUE ELECTRONIQUE

POUR IDENTIFIER LES DENREES IONISEES

Louis SAINT-LEBE et Jacques RAFFI

Après avoir décrit le principe de la résonance paramagnétique électronique et les conditions qu'elle requiert afin d'être utilisée dans l'identification des denrées ionisées, on décrit les résultats déjà publiés. A l'aide de deux exemples (céréales et pruneaux irradiés) sont alors recherchées les possibilités de développement de cette méthode.

A POINT OF VIEW ABOUT IDENTIFICATION OF IRRADIATED FOODS

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Irradiation of food is one approach for reduction of food losses or for improvement of their nutritional quality. This treatment, though still prohibited in certain countries, is now legal in many others, since the joint FAO/IAEA/WHO Expert Committee concluded in 1980 that "the irradiation of any food commodity up to an overall average dose of 10 kGy presents no toxicological hazard" (ANONYMOUS, 1981). In order to prevent illegal imports of irradiated foods, and control the authorized foodstuffs, it would be desirable to be able to determine by examining the food :

- whether the food has been irradiated or not,
- and if so, at what dose.

Various methods should be discussed, including luminescence techniques, impedance measurements, specific radiolytic products investigation, microbiological methods; only electron spin resonance (ESR) studies will be considered here.

1) ESR : Principle and conditions required for its use in identifying irradiated foods

(see for instance WERTZ and BOLTON, 1972 or BORG, 1976)

An ESR experiment consists in measuring the attenuation of a beam of electromagnetic radiation passing through a sample of matter, as a function of the strength of the magnetic field applied to this sample. The derivative of the absorption is, in fact, recorded. Lines or bands in a spectrum are relative to transitions between energy levels of an odd electron ; thus ESR spectroscopy is only applicable to systems with net electron spin momentum ; many systems, however, fulfill this condition : points defects in solids, excited triplet state, most transition-metal ions, free radicals ; ESR may be used to determine chemical kinetics involving single electron transfert (oxidoreductions), chemical activities at various atomic sites on free radicals, aspects of crystalline structure and of certain properties of conduction and semi-conduction.

As ionizing radiations create radicals in food, the idea to explore the possibilities of ESR is not new. Before reviewing the literature let us note that induced ESR signals must fulfill several requirements :

a) they must be stable, or fairly stable compared to the usual time storage of the foodstuff ; since radicals are destroyed by reaction with one another or with other molecules, particularly water, this is only true in solid phase ; this may either the state of the whole food or the particular part of the foodstuff where ESR signals can be recorded ;

b) they must be clearly distinguishable from the signals given by the unirradiated sample, whether it is heated or not, even after a long time storage (see point a);

c) their concentration must be proportional to the irradiation dose if you also want to estimate the dose. The radical concentration therefore be stable in any conditions to which the sample may be submitted (heat treatment, for example), and relatively homogeneous throughout the medium. ESR recording conditions must also be satisfactory for the purpose (no saturated signals).

In order to characterize the ESR signal, the following parameters are often measured (Fig.1) :

- the g-factor, which is relative to the "center" of the spectrum, calculated by the formula :

$$g = hf / \beta H_0$$

where "f" is the electron resonant frequency, "H" the central field (often measured at the intersection between the base line and the ESR signal), "h" the Planck's constant and "β" the Bohr magneton. In practice :

$$g = 714.484 f(\text{GHz}) / H_0(\text{G})$$

- the peak-to-peak width "ΔH", measured as shown on figure 1 on the recorded first-derivative curve, is also related to the width of the absorption curve.

- the most accurate method of following the decay of the signal intensity is to integrate the full absorption curve (from two consecutive integrations from the recorded first-derivative curve). This is tedious and often impossible; however, the intensities of the different signals may be approximately obtained from the formula :

$$I \sim Y_{\text{max}} (\Delta H)^2$$

in which Y_{max} is the peak-to-peak derivative amplitude (Fig.1). Thus, the radical concentration decay may be followed by measuring Y_{max} at constant amplification gain.

2) LITERATURE REVIEW

2-1- Though a great deal of data has been published on the identification of irradiated foods, that's saying a lot there is only a few articles on ESR proof of irradiation, the most important being that of DODD et al. (1985); moreover, most of this literature concerns dosimetry problems or general data (REGULLA and DEFFNER, 1982 ; McLAUGHLIN et al., 1983 ; ZUPPIROLI et al., 1985 ; HASSELMANN et al., 1986).

On the other hand, numerous "fundamental" ESR studies have been carried out on irradiated food or food components (TAUB, 1981 ; BOUHARY et al., 1983 ; RAFFI and AGNEL, 1983 ; SEVILLA et al., 1983); (for instance more than 250 on sugars ! Let us also note that ESR spectroscopy is also used in other cases like UV-radiation (RAYSHIN et al., 1975 ; KUBOTA et al., 1975 ; MERLIN and FOUASSIER, 1980 and 1982), heating (ARTHUR and HINOJOSA, 1966 ; GUTSZE, 1977 ; MROZOWSKI and GUTSZE, 1977 ; SANTANILLA

et al., 1981 ; DOYLE and LODNEY, 1982 ; SIMKOVIC et al., 1986), chemical reactions (HAYASHI and NAMIKI, 1981 ; EVANS et al., 1984), mechano-radicals (SOHMA and SAKAGUCHI, 1975 ; KUDO and HEUSINGER, 1982), presence of enzymes (BORG, 1976) and mixtures of sugars and metaloxides (KASHIWAGI et al., 1979).

2-2- DODD et al. have recently published interesting data concerning ESR proof of irradiation ; they first showed that " ESR appears to be an excellent method for any foodstuff containing bone or cuticle " like meat, fish or crustacea; they used doses in the range of 4 to 10 kGy but estimate that the irradiated sample can be distinguished even at doses of 200 Gy; however the storage is not studied more longer than 3 weeks. They also studied excised strawberry achenes and showed how the ESR signal of the irradiated samples may be distinguished from that of unirradiated fruit (ESR lines due to Mn^{2+}). These findings are important, in view of the pessimistic earlier reviews (TRUBY, 1957 ; ONDERDELINDEN and STRACKEE, 1970 and 1973) and also experiments cited by DODD et al. on spices and papayas (BECZNER et al., 1973), though cases of very long-lived radicals are known and used for archaeological dating (IKEYA and MIKI, 1980 ; OSTROWSKI et al., 1980).

2-3- Though proof of irradiation by lyo- and chemiluminescence will not be discussed here, we mention them briefly since ESR and lyoluminescence (LL) (light emitted on dissolution of pre-irradiated solids) have been supposed or proved to be linked.

Luminescence is not specific to gamma radiation (WARD and BENERITO, 1983) nor to sugars, as aminoacids also lead to LL (ETTINGER and BUCHAN, 1979 ; ETTINGER et al., 1982) but sugars have been specially studied : mannose (BARTLETT, 1979 ; BARTLETT and BROWN, 1979 ; BARTLETT et al., 1982), lactose (MATYUSHKOV et al., 1983) and trehalose (ATARI, 1985) for example. Both ESR and LL are related to long-lived species present in irradiated samples but there seems to be no general correlation between the free radical concentration, measured by ESR, and the observed LL intensity : in case of mannose, the spin concentration did not saturate until a dose of about 100 kGy, almost three orders of magnitude higher than the saturation dose for LL (BARTLETT, 1979), differences being thus most apparent for samples irradiated at high doses but also with products stored for long periods in air (BARTLETT and BROWN, 1979) although atmospheric oxygen plays no major part in the processes which take place in the solid (BARTLETT et al., 1982).

On the other hand, a relationship was found between chemiluminescence (CL) and ESR in plasma irradiated saccharides (WARD and BENERITO, 1983) and CL intensity could be predicted if the ESR intensity was known, in the case of the sugars studied (various celluloses, glucose, maltose,...).

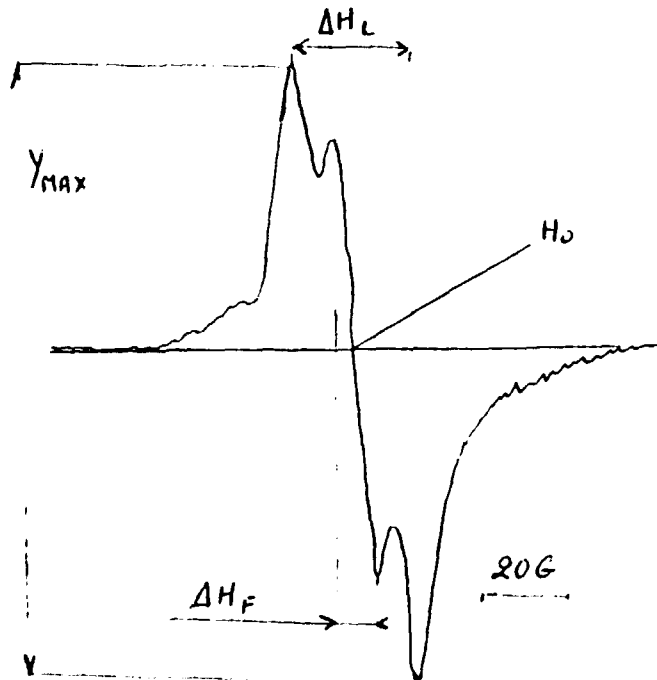
Thus much further work needs to be carried out in this field but comparative ESR and LL studies should lead to better understanding of the relative phenomena and may offer the best chances of success in providing a proof of irradiation.

3) EXAMPLE OF IRRADIATED CEREALS

Studies have been carried out on cereals in the past (EHRENBERG and EHRENBERG, 1959; LEF and CHEN, 1965) but without success in order to prove irradiation. Since recent data has appeared on the gamma radiolysis of starches (HENDERSON and RUDIN, 1981; RAFFI and AGNEL, 1983), we decided to continue work on cereals such as bread-wheat, barley and maize, and on bean and soya for comparison. These products were irradiated in the usual conditions (i.e. in air and at room temperature) at doses of 0.3, 5 and 10 kGy delivered by a cesium 137 cell (activity : 18600 Ci; dose rate : ~ 3.6 kGy/h).

Spectra were recorded at room temperature, contrary to the experiments of EHRENBERG et al. (1969), using a 200 D10 BRUKER ESR spectrometer combined with an ASPECT 2000 computer.

Figure 1 : ESR spectrum of barley, recorded just after a 5 kGy irradiation (medium field $H_0 = 3470.5$ G).



ESR spectra of irradiated samples (Fig.1) essentially consist of two signals, one "fine" ($\Delta H \sim 8.6$ to 11.4 G), and the other "large" ($\Delta H \sim 20.4$ to 23.7), except in the case of bean, in which only the first signal ($\Delta H = 9.4$ G) is detected. Unirradiated products always show a very weak signal (sometimes approaching the limit of detection and thus needing accumulation by computer), the peak-to-peak width ($\Delta H \sim 8$ to 13 G) or the g-factor of which can lead to confusion with signals from irradiated samples; on the other hand, it is readily distinguished from the large ESR line, when this latter is observed.

If these results are to be used as valid proof of irradiation, the spectrum must be discernable, even after a long period of storage. Thus, the decrease of the lines with time, was

followed at room temperature, for each dose. Kinetic curves were drawn for the two highest doses (5 and 10 kCy). We can assert that :

- the initial concentrations are not directly related to the irradiation dose, except in the case of maize. This is not due to a saturation of the ESR signal, since proportionality is found in the case of maize; the problem is rather one of homogeneity, whole grain being used for these experiments; soya, barley and wheat grains, being small enough to be put in the ESR tube, were used directly, despite subsequent inhomogeneity which prevents quantitative comparisons between different samples but allows the kinetics of disappearance of the signal to be studied. On the other hand, the maize grain, being too big, had to be ground, despite the risk of destroying some of the radicals (by heating caused by grinding) and of initiating new "mechanical" radicals; this method, however, gave a very good homogeneity in the different samples.

- the initial heights of signals are always significantly greater than those of non irradiated samples.

- the kinetic curves of disappearance (Fig.2) of ESR signals present, on semi-log scales, two straight lines, the slopes of which are, in the case of the three cereals, very close to those found in case of starches (RAFFI and AGNEL, 1983). This is not surprising as the starch content represents about 70 to 80 % of these three cereals. To compare with values given in table I, the ESR and kinetic constants of starches are as follows:

- large (and initially main) signal:

$g \sim 2.004$ to 2.006 and $\Delta H \sim 19.2$ to 26.1 G

- fine signal:

$g \sim 2.03$ to 2.006 and $\Delta H \sim 8.2$ to 9.3 G

- the kinetic constant of the first straight line being proportional to the water-content W for the fine signal (and to W^2 for the large one) with $K \sim 450 \cdot 10^{-3}$ (day) for all starches with $W \sim 12-15$ %. The second slopes are either independent of W and the starch and equal to 34 and $68 \cdot 10^{-3}$ (day) respectively for fine and large ESR signals. We can thus conclude that the radicals found in these cereals are mainly due to their starch. Those results need to be improved by other experiments on various cereals; we should also check that higher storage temperatures (as encountered in the Third World) do not destroy the ESR spectra too rapidly; however, we might show relatively optimistic as the starches irradiated in 1980-1981 for the study cited above always show ESR spectra at present time, i.e. six years later. We thus hope to obtain a valid test for irradiation at least for higher doses; but we can assert that determination of the irradiation dose will be impossible, as the length of storage time will not always be known.

Figure 2 : Decrease of the logarithm I of the radical concentration (arbitrary units) in barley as a function of the storage time T (in days) :

- "fine" signal : holed (5 kGy) and full (10 kGy) circles
- "large" signal : squares (5 kGy) and full triangles (10 kGy)

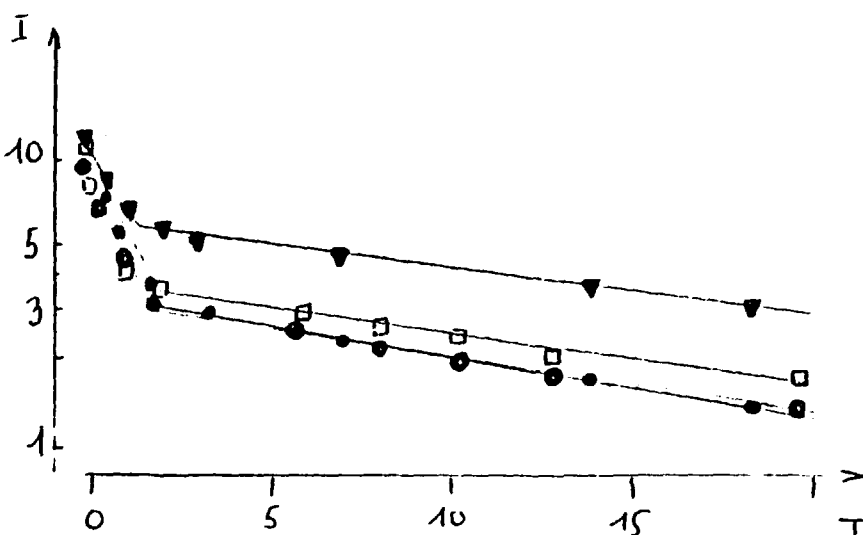


TABLE I : ESR and kinetic Constants of observed signals.

Product	Bread-wheat	Barley	Maize	Soya	Bean
NON-IRRADIATED SAMPLES					
g	2.015	2.02	2.01	1.99	1.99
$\Delta H(\pm 0.3G)$	8.7	8.1	8.5	13	9
FINE SIGNAL					
g ^a	2.015	2.01	2.01	1.985	2.01
$\Delta H(\pm 0.3G)$	8.7	8.6	9.5	11.4	9.4
K1 ^b	420	490	590	400	740
K2 ^b	95	50	80	150	70
LARGE SIGNAL					
g ^a	2.015	2.01	2.01	1.985	2.01
$\Delta H(\pm 0.5G)$	21.3	23.7	20.4	21.7	?
K1 ^b	400	410	680	500	
K2 ^b	130	35	115	145	

a = average value of g-factors of fine and large signals
 b = in 10³ (day)

EXAMPLE OF FRENCH PRUNES

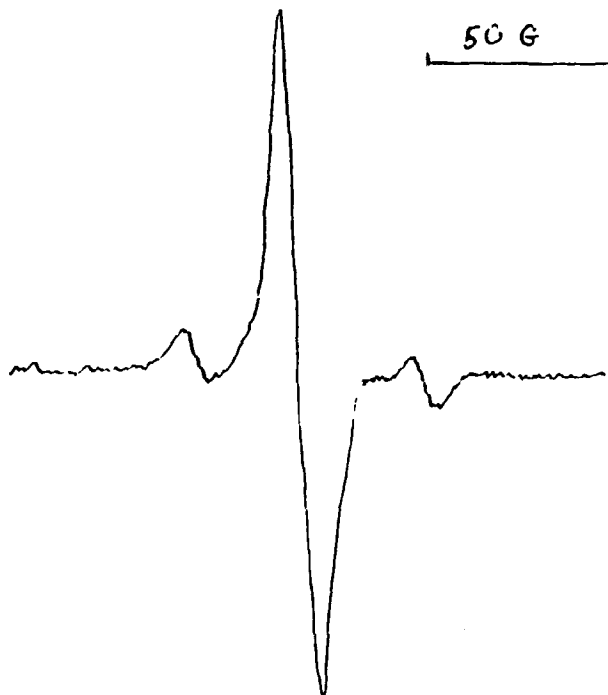
We carried out the same experiments with French prunes, determining the g-factor, peak-to-peak width and radical concentration. No signal was found in the pulp, the study thus only concerns the prune stone, in which both irradiated and non irradiated samples gave an ESR spectrum :

- the non irradiated sample showed a spectrum which consisted essentially of an apparent singlet of $g \sim 1.92$ and $\Delta H \sim 7.6$ G;

- the irradiated samples gave a complex signal (Fig.3) composed of at least two lines: the first is an apparent singlet, the g-factor of which may be less than that of the unirradiated sample ; its width appears to vary with the dose from 8.1 (0.4 kGy) to 9.1 G (10 and 15 kGy); these two singlets are probably of different origin, but not differ sufficiently to be distinguished without doubt. The second signal is a doublet (60.9 G between the two lines) or a triplet, whose g-factor is approximately the same as those of the other two signals. Here, there is no ambiguity and it is impossible to mistake this doublet (or triplet) for the singlet of the non irradiated prune stone.

- this ESR signal rapidly decreases with time and this result leads us to be suspicious to a possible use of ESR in an irradiation proof; nevertheless, further experiments remain to be carried out.

Figure 3 : ESR spectrum of french prune stones irradiated at 5 kGy (medium field : 3494.5 G)



CONCLUSION

The ESR method is rapid (only a few minutes), may be non destructive and requires only about 100 mg of materials. If it is to be used as an official proof that a product has been irradiated, however, it needs to be further developed: the two examples discussed above (cereals and French prunes) show the problems which have to be solved. The most important deterrent, however, remains the fact that proof of irradiation mainly concerns manufacturers, health authorities, legislators and applied research laboratories - not generally equipped with ESR spectrometers -, whereas laboratories which have ESR apparatus do fundamental research and consequently have no special interest in food irradiation.

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