FREE RADICAL MEASUREMENT IN BIO-ORGANIC SUBSTANCES USING AN ELECTRON SPIN RESONANCE TECHNIQUE

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ABSTRACT

Electron spin resonance (ESR) is a simple, rapid and reliable method to measure absorbed doses in tissue-equivalent bio-organic substances, particularly amino acids and sugars or biological samples such as teeth, nails, hair and bone, as well as items of clothing, jewellery, medication or confectionery. In this capacity ESR represents a useful adjunct to existing dosimeters in cases of retrospective monitoring of radiation accidents, inadvertent radioactive releases or contamination and other emergency or operational situations. Studies have been performed to establish the dose and dose-rate responses, energy dependence, minimum detectable dose limit, post-irradiation stability of the ESR signal, and the practical limits of sensitivity, reproducibility and quantitation.

INTRODUCTION

Free radicals formed by irradiation are trapped in solids, and their number is proportional to the absorbed dose. ESR signals from bone, teeth, nails and hair have been used in biological dosimetry to estimate the absorbed dose in the human body, but poor sensitivity, stability and reproducibility have limited their application (1). An alternative approach is to study the ESR signals in tissue-equivalent substances or man-made items generally found associated with or in close proximity to humans, which can act as surrogates in emergency dosimetry for estimating human exposure (2). We have studied the ESR spectrometry of irradiated sugars and compared their response with other bio-organic substances and biological samples.

EXPERIMENTAL METHODS

Various irradiated samples (200-300 mg) were placed in a quartz tube (4 mm ID) and exposed to microwaves (10 mW power) at an X-band frequency (9.6 GHz) inside a microwave cavity between the poles of an electromagnet (330 mT field), in a Varian E-109 spectrometer, and the ESR spectrum determined by scanning over a field range of 3.3 ± 0.01 mT.

The ESR machine was calibrated daily against strong pitch, and the ESR signals from irradiated samples were measured against an internal reference spectrum of Mn^{2+} (7.7 μmol L^{-1} solution sealed in a 1 mm ID quartz microtube). Signal strengths were determined either as peak-to-peak heights or as areas under the second-derivative curve, and

by taking the average of at least three measurements per experiment, an estimated precision of ± 10% is obtained.

RESULTS AND DISCUSSION

Most forms of radiation dosimetry have limitations (3,4) for retrospective estimates of accidental (acute) or occupational (chronic) exposure. Biological and biochemical indicators (5) show some individual variability and fluctuations in the lack of a reliable base-line reference point prior to irradiation; most changes are short-term with indeterminate time-dependent responses. Cytogenetic methods are quite sensitive but require specially trained and highly skilled operators to perform the complex analyses (5).

The remaining methods are biophysical and include ESR dosimetry (1), lyo- and thermo-luminescence(6), spectrophotometry, densitometry and radiography (Table 1). Excluding LiF crystals and sensitive X-ray film, which would not normally be present at the scene of an accident prior to irradiation, emergency dosimetry must often rely on commonly available materials or readily obtainable biological samples, and ESR dosimetry is the only technique that can be used with such a wide range of materials (1,5).

Table 1: Biophysical Dosimetry

Sample	Method*	Dose Range Gy
Amino acids	ESR	$1-10^5$
Sugars	ESR	$1-10^5$
Amino acids	Lyoluminescence	$10-10^6$
Sugars	Lyoluminescence	$10-10^6$
LiF	Thermoluminescence	$10^{-5}-10^5$
Plexiglass	Spectrophotometry	10^3-10^6

* Precision ± 5%.

Biological samples suffer from irreproduciblity, and consequently we have concentrated on universally available tissue-equivalent granulated table sugar (sucrose) as a suitable material (2). The ESR signals obtained following irradiation are simple, stable and reproducible, with a lower limit of detection of ~0.5 Gy, a linear dose response up to very high doses ($\geq 10^4$ Gy), independent of dose-rate and photon energy. This, combined with the universal application of ESR dosimetry to foodstuffs, human samples and bio-organic substances (Table 2), the ease of collecting and handling samples, their post-irradiation signal persistence and stability (Table 3), and the straight forward and rapid non-erasive measurement capability, make ESR a useful biophysical dosimeter for a variety of radiation applications including radiation processing,

polymerization and vulcanization of rubber, waste treatment, food irradiation, sterilization of medical supplies as well as for emergency dosimetry.

Table 2: ESR Signals from Irradiated Biological and Bio-organic Samples*

Category	Sample	Signal Intensity.g^{-1}	Relative Sensitivity
Grains and spices	Flour-bleached	0.07	0.0
	Rye	3.70	0.05
	Wheat	4.35	0.05
	Popcorn	8.14	0.09
	Cinnamon	3.75	0.05
	Pepper-black	8.73	0.10
	Rice-long grain	6.69	0.07
Biological samples	Teeth-crushed	22.65	0.25
	Human finger nails	50.09	0.59
	Human Hair black	53.00	0.59
	Human Hair grey	42.78	0.48
Bio-organic samples	Sugar-granulated	77.27	0.86
	RTV+ bound	89.89	1.00*
	Placebo	150.12	1.73
	Alanine-paraffin pellet	157.65	1.75

*10 Gy absorbed dose.
+Signal normalized to Dow Corning RTV Silicone pellets containing sucrose.

CONCLUSIONS

ESR spectrometry can be used as a biophysical dosimeter to measure absorbed doses $\geq$0.5 Gy in bio-organic substances (alanine, glucose) and biological samples (hair, nails). The ESR signals are directly proportional to absorbed dose, independent of dose-rate and photon energy (50-1250 kV), and stable for long periods after irradiation.

Table 3: ESR Dosimetry Using Biological and Biochemical Indicators.

Indicator System	Target Organs	Bioassay Site	Dose Range Gy	Time Period of Applicability After Exposure
Hair	whole-body partial body	hair	1 - 4	days/weeks
Nail	partial body	nail	1 - 4	days
Tooth	whole-body oral cavity	tooth enamel	0.5 - 5	years
Bone	whole-body	bone	0.5 - 5	years
Sugar Crystal	-	-	≥ 0.1	months
Organic Molecule (alanine)	-	-	≥ 0.1	months

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