Retrospective dosimetry with EPR and OSL at McMaster University

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Abstract

Retrospective dosimetry may be of use following a radiological incident, in order to determine whether individuals may have been exposed. We briefly review the fundamentals of two primary techniques for retrospective biophysical dosimetry: electron paramagnetic resonance (EPR) and optically-stimulated luminescence (OSL). Our facility at McMaster University has the capability to perform both EPR and OSL dosimetry, which provides us with the flexibility to study so-called "fortuitous" dosimeters with the most appropriate technique. In this paper, we review our research of the past decade, during which we have developed techniques for the measurement of absorbed dose in human, rodent, and canine dental enamel, synthetic quartz oscillators, and gypsum wallboard.

1. Introduction

Retrospective dosimetry is the measurement of absorbed dose in "natural or locally available materials" [1], which may be contrasted with dosimetry that uses synthetic (commercial) dosimeters. Retrospective dosimetry may be utilized to determine doses following radiological accidents, for the purposes of triage or to manage the response to the accident. For example, sugar samples were collected from buildings near a junkyard in Samut Prakarn (Thailand) following a 19-day exposure to a dismantled ^{60}Co source; the absorbed dose to the sugar was shown to be less than 300 mGy [2]. In addition, retrospective dosimetry has been applied following the Goiâna (Brazil) [3], JCO (Japan) [4], [5] and other radiological incidents.

Sample preparation and analysis techniques have been published by the IAEA for ESR measurements of dose in human tooth enamel samples [6]. However, it is difficult to envision obtaining human tooth enamel samples following a radiological emergency, which has prompted research into other approaches to retrospective dosimetry. Both electron paramagnetic resonance and optically-stimulated luminescence are techniques of physical dosimetry that may be utilized with so-called "fortuitous" dosimeters.

In this paper, we discuss the retrospective dosimetry capabilities at McMaster University and review recent research involving retrospective dosimetry with electron spin resonance and optically-stimulated luminescence dosimetry.

1.1 Electron paramagnetic resonance (EPR)

Electron paramagnetic resonance (EPR), often called electron spin resonance (ESR), is a well-known spectroscopic technique for the study of free radicals and point defects. Radiation-induced free radicals were studied as early as 1955 [7], [8]. Applications of EPR dosimetry current include transfer dosimetry with alanine, geochronology, and retrospective or forensic dosimetry [9].

EPR may be illustrated with the model of a free electron in a magnetic field (Figure 1). With application of an external magnetic field, the degenerate energy state splits into spin-up and spin-down levels (Zeeman splitting). At resonance, incident microwaves may induce a transition from the lower to upper energy state via absorption of a photon. Alternately, incident microwaves may induce a transition from the upper to the lower energy state via stimulated emission. In a population of isolated spins, the lower energy state will be more populated, so that net absorption is possible. EPR scans are typically performed in the field-swept mode, in which the microwave energy (frequency) is constant, while the external magnetic field is swept. At resonance, the magnitude of the undistorted absorption signal is proportional to the number of spins. For reasons of experimental convenience, the experimenter typically measures the first harmonic (first derivative) of the absorption signal. For additional details, see [10].

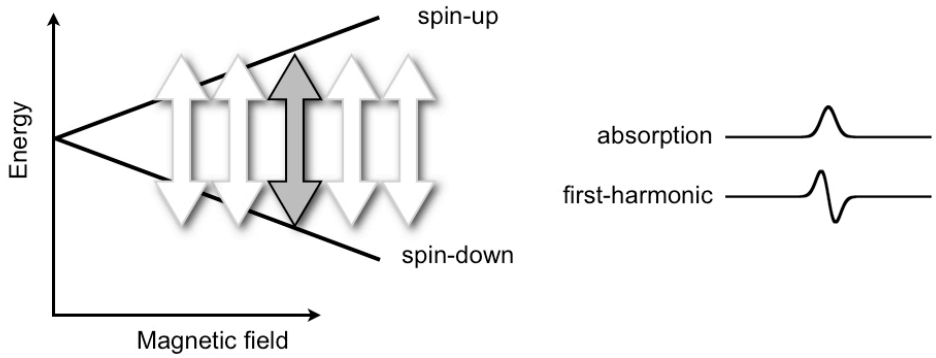

Figure 1. (left) An external magnetic field splits the energy state of a free electron into spin-up and spin-down levels. Microwave photons may induce transitions between the levels when the magnetic field is such that the level separation is equal to the photon energy (resonance). (right) The absorption and first-harmonic spectrum of a single, isotropic EPR line.

1.2 Optically-stimulated luminescence (OSL)

Optically-stimulated luminescence (OSL) was developed from thermoluminescence (TL). Electrons which are trapped at sites in the bandgap of a semiconductor may be released through "optical" stimulation (where "optical" refers to ultraviolet, infrared, as well as visible wavelengths) [1]. Upon release, the electrons may conduct through the material before recombining at a charge-compensating site. This recombination may be accompanied by the emission of light: hence, optically-stimulated luminescence.

OSL may also be used for dosimetric purposes. Radiation causes electrons and holes to be trapped at various defect sites in a material, and stimulation results in the emission of light, for which the intensity may be proportional to absorbed dose.

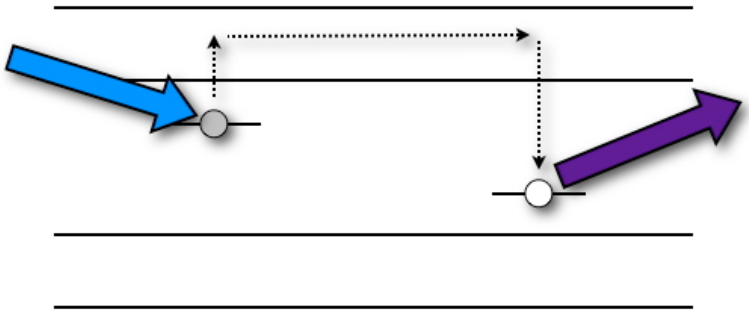

Figure 2. Schematic of the OSL process. Charge is trapped at defect sites with energy states intermediate between the valence and conduction bands. Optical stimulation (blue arrow) results in absorption, conduction, and recombination with emission (purple arrow).

1.3 Comparison of EPR with OSL dosimetry

EPR and OSL are related techniques, in which the quantity of "trapped" charge is related to the absorbed dose. However, the nature of the traps which may be observed with either technique result in very important practical differences between EPR and OSL dosimetry. In this section, we briefly review some relevant points of comparison.

1.3.1 Destructive and non-destructive measurements

EPR measurements are intrinsically non-destructive. The population of trapped spins is not affected by the measurement process, which involves only the transitions between spin states. In contrast, OSL measurements irretrievably depopulate the traps. However, it is possible in some cases to make very short or pulsed OSL measurements, which do not significantly affect the population of trapped charges. For both EPR and OSL, sample preparation (not the measurement) may be destructive.

1.3.2 Light sensitivity

OSL signals are generally quite sensitive to sunlight or laboratory lighting; this is inherent in the physical process of optically-stimulated emission. The free radicals observed with EPR may or may not be sensitive to light. In cases where significant light exposure is associated with a possible fortuitous dosimeter, EPR is likely to be a more successful technique.

1.3.3 Aliquot size

The sample mass required for EPR is frequently on the order of 100 mg, while OSL aliquots are typically less than 10 mg. Single-grain analysis of OSL dosimeters (quartz, Al_2O_3:C) is largely routine but remains an extraordinary challenge for EPR.

1.3.4 Experimental considerations

Commercial OSL readers are very convenient to use. Many aliquots (e.g., 48) may be mounted in the reader at the same time, and the measurement process is controlled through software. On-board ß-irradiators allow for dose-response curves to be measured for individual aliquots, and internal

heaters permit suitable pre-heating protocols which are used to eliminate spurious signals resulting from very shallow, unstable traps.

In contrast, commercial EPR spectrometers require much more user intervention. Although automated sample changers do exist, they are not in routine use. Also, on-board irradiation is not available. Thus, dose-response curves can only be measured if aliquots are processed at an irradiation facility. Single-aliquot dose-response curves require several iterations of EPR measurements and external irradiations.

1.3.5 Summary

The experimental convenience provided by a commercial OSL reader is extremely attractive. However, we must emphasize that the traps available in a potential fortuitous dosimeter may be accessible to only one of either EPR or OSL. McMaster University houses one of the few laboratories equipped with both EPR and OSL equipment, which provides us with the flexibility to study materials with the most appropriate technique.

2. Progress with EPR dosimetry

2.1 Tooth enamel

CO_2^- radicals form in dental enamel (primarily hydroxyapatite) upon irradiation [11]. As the EPR signal from these radicals is extremely stable, it is not necessary to make dose measurements immediately following exposure. However, it may be difficult to obtain human dental extracts for the purposes of dosimetry. In addition to procurement, additional challenges include the effect of dental disease, cumulative exposure to medical x-rays, and exposure to UV light (which induces an interfering signal). Nonetheless, dental enamel is arguably the best biophysical dosimeter, and correspondingly the McMaster EPR laboratory has focused much of its research on dental enamel. We review some of our research results from studies of human, rodent, and canine dental samples.

2.1.1 Human teeth

We have developed a procedure for dose measurement in human tooth extracts (obtained from a dental clinic) [12]. Dental enamel is separated from the underlying dentine tissue through treatment with supersaturated KOH. In order to reconstruct low doses, it is necessary to fit the acquired EPR spectra with functions that represent both the native, pre-irradiation signal and the radiation-induced signal. Doses as low as 100 mGy can be obtained. The uncertainty is roughly ±50% at this level; accuracy improves to within ±5% at less than 1000 mGy.

In addition, we have studied the response of human tooth enamel to neutron irradiation . Enamel was shown to be approximately 1/10 as sensitive per Gy for neutrons when compared to gamma irradiation [13]. This would appear to limit human enamel dosimetry for whole-body neutron exposures to post-mortem studies.

2.1.2 Rodent and canine teeth

As human survivors of a radiological emergency may not be willing to provide samples of tooth enamel, it was proposed that rodents and dogs may serve as a potential source of enamel [14]. Laboratory doses have been successfully measured in mice molars, but reduced sensitivity of rodent

enamel and the small quantity of available enamel limited the minimum detectable dose (1400 mGy).

Similarly, canine teeth have been shown to be suitable biophysical dosimeters [15], with a minimum detectable dose of approximately 200 mGy. Similar procedures could be applied to feline enamel samples.

2.2 Wallboard (drywall)

Gypsum wallboard (drywall), a nearly-ubiquitous construction material in North America, was proposed as an emergency EPR dosimeter by [16]. Recently our laboratory has undertaken an extensive effort to characterize wallboard as both an EPR and OSL dosimeter. Both CO_3^- and SO_3^- radicals have been produced through gamma irradiation of local wallboard samples. The CO_3^- radical provides the maximum signal intensity, and therefore has been the focus of our subsequent EPR research.

An initial project [17] involved the irradiation of a wallboard panel by a line source (^{60}Co), providing a spatial distribution of doses (2-110 Gy). Samples were extracted from the wallboard, and the EPR signals intensities were converted to doses, providing a spatial "map" of the irradiation (see Figure 3).

Before we can state that wallboard is suitable as an emergency dosimeter, it is necessary to compare the dose sensitivity across a variety of samples. The gypsum itself is either mined from various natural sources or produced synthetically at coal-fired power plants. The different gypsum sources may yield unique combinations of parent defect sites that will be converted to paramagnetic centres upon irradiation, as well as varying levels of dose-insensitive background signals

Our laboratory recently undertook a study of wallboard sampled from locations across the United States and Canada. The preliminary results shown in Figure 4 clearly indicate that different samples of drywall yield different sensitivities to dose. In addition, we are currently attempting to reduce the detection limit through careful measurements of the background spectrum.

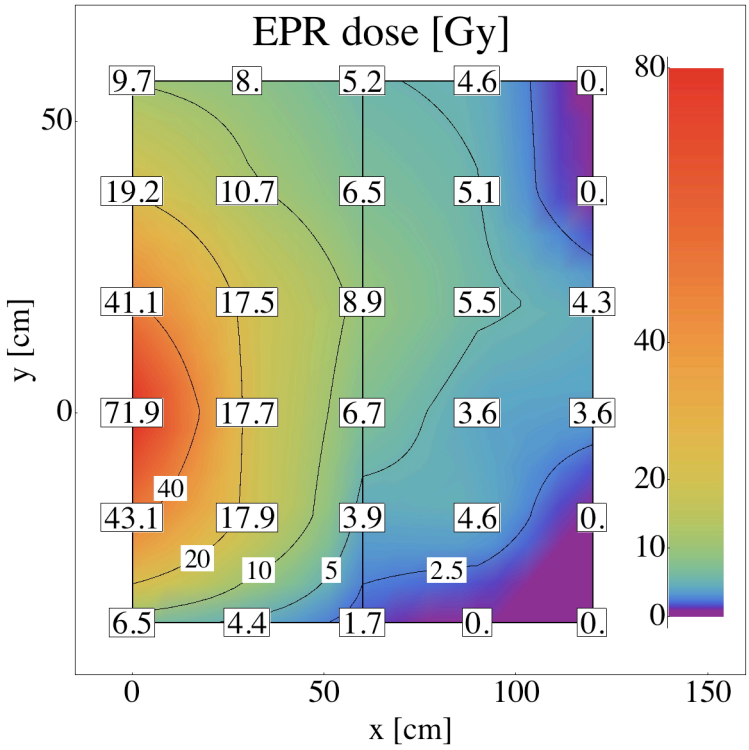

Figure 3. Spatial "map" of absorbed dose measured in wallboard panels. A line source (^{60}Co) was held perpendicularly to the panels. Measured doses are shown in boxes. Shading and contours were determined through interpolation. After [17].

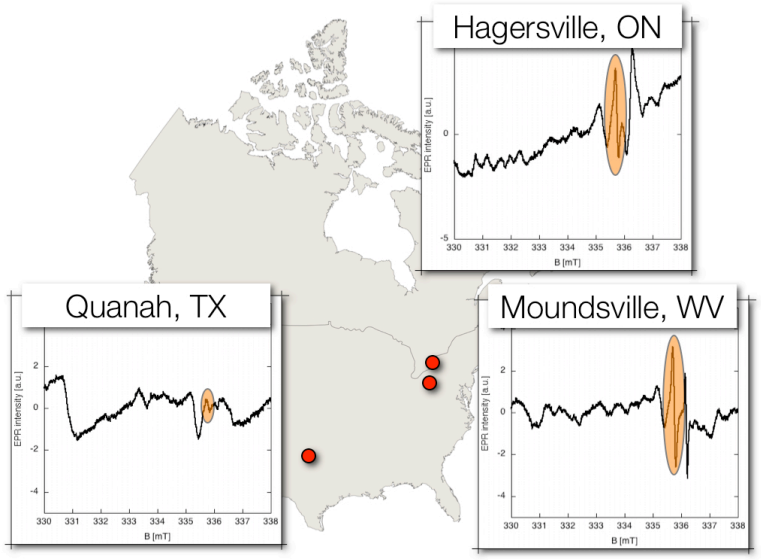

Figure 4. EPR spectra for irradiated wallboard (20 Gy) from three different manufacturing facilities. The radiation-induced CO_3^- signal of interest has been highlighted in orange.

2.3 Whewellite (calcium oxalate monohydrate)

Whewellite forms as a thin oxalate crust on carbonate surfaces, such as marble and limestone, as a result of secretions by lichens. A study of synthetic whewellite indicated the presence of a very strong, relatively stable dose-sensitive EPR signal [18]. Unfortunately, irradiation of natural whewellite obtained from an external wall (as well as samples from geologic contexts) yielded no observable EPR signals with doses as large as 50 Gy. Although the difference between synthetic and natural whewellite has not been explained, we have not pursued additional research with this mineral.

2.4 Foodstuffs (brown sugar, coffee)

The EPR laboratory has also been utilized in undergraduate research projects. One recent project (unpublished) demonstrated that brown sugar was dose sensitive between 0 and 15 Gy, although a confounding background signal (presumably from molasses) will certainly interfere with accurate dosimetry below a few Gy. The same project investigated instant coffee, but found no useful dose-sensitivity over the same dose range.

3. Progress with OSL dosimetry

3.1 Synthetic quartz

Synthetic quartz oscillators are present in a variety of personal and household items, including wristwatches, cellular telephones, and clocks [19]. A recent study of synthetic quartz oscillators concluded that these could be useful as emergency dosimeters, provided the oscillators were sensitised prior to use through a combination of heating (800° C) and serial irradiations with lower-temperature annealing. With the proper sensitisation, reliable measurements (±10%) of dose can be made with applied doses of 500 mGy.

3.2 Wallboard

Having characterized wallboard dosimetry with EPR, we turned to OSL as a potential technique for the measurement of dose [20]. Although the experimental convenience of OSL is very attractive, the results were not wholly promising.

A radiation-induced luminescence signal was observed in irradiated wallboard. However, this signal was very weak compared to an interfering “natural” signal that was present in non-irradiated wallboard (Figure 5). Although challenging, it is possible to separate the radiation-induced from the natural signal. The radiation-induced trapped charges have a larger photo-ionization cross-section, and thus are preferentially released at low stimulation powers. We were able to develop a technique of dose measurements using individual aliquots (~8 mg) of wallboard and suitable sequences of stimulation and irradiation.

Unfortunately, the radiation-induced OSL signal decays rapidly, with complete erasure observed within days. This places a strong limit on the utility of wallboard as an emergency dosimeter. However, the rapid decay may also be used to advantage: our collaborators at the DRDC have been investigating a variety of materials for use in forensic dosimetry [21]. In this case, the radiation-induced luminescence signal would be a clear marker of a previously-hidden illicit radioactive source. Combined with EPR measurements, it may be possible to determine a time of irradiation in some cases.

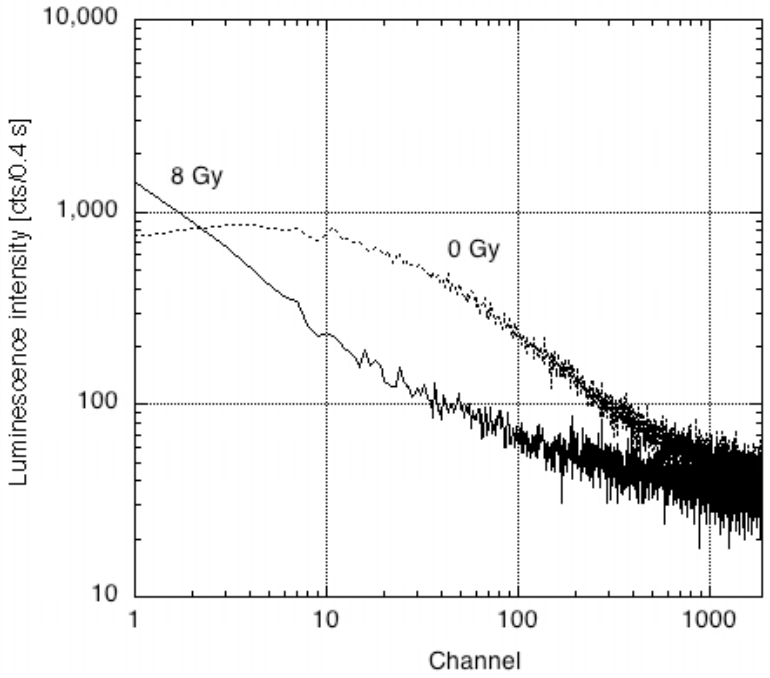

Figure 5. Optically-stimulated luminescence shinedown curves for irradiated (8 Gy) and unirradiated wallboard (90% stimulation power).

3.3 Improvements in measurement protocols

Although OSL dosimetry is typically very experimentally convenient, the time needed to acquire the necessary data for a single sample can be quite large (hours or days). To obtain adequate precision for dose measurements on a single sample, it is often necessary to acquire data on large numbers of aliquots (24, 48 or more). For each aliquot it is necessary to perform several sequential steps of measurement, irradiation, and calibrated heating. Depending on the investigation, it may take days to acquire enough data to measure even a single dose with adequate precision (see, for example, [20]).

We developed a Monte Carlo simulation of the measurement procedure that may be useful in addressing this issue [22]. Under reasonable assumptions regarding the uncertainty in the luminescence measurement, it was shown that the number of steps required to obtain a reasonable estimate of dose could be reduced by 50% in some cases. Although the results of this simulation have yet to be compared with experimental data, they do suggest that significant savings in time is possible. This may be particularly important for triage, in which samples must be processed

sequentially on a limited number of OSL readers. There is a clear opportunity for significant additional research regarding protocols that allow rapid estimates of absorbed dose.

4. Future directions

We recently obtained pilot funding for a preliminary study of EPR dosimetry of textiles. Early reports of retrospective dosimetry of textiles were very promising and suggested a minimum detectable dose of 1000 mGy in cotton and 500 mGy in polypropylene [23][24][25][26]. However, this early work was not pursued.

Our pilot funding has allowed us to place an order for an EPR sample goniometer, which is used to rotate the sample during EPR measurements. This will compensate for the effects of anisotropy in the sample fibres, which have so far stymied our attempts to observe a reliable dose-sensitive signal in textiles. We hope to replicate these very exciting initial results and develop additional research based on this pilot study.

5. Conclusion

We have reviewed research results obtained at the McMaster EPR and OSL laboratory regarding applications of EPR and OSL retrospective dosimetry. Initial work focused on the development of dose measurement techniques utilizing human tooth enamel extracts. Later, we demonstrated it was possible to perform retrospective dosimetry using canine and rodent dental samples, which may be a more practical approach to dosimetry following a radiological incident. Quartz oscillators were shown to be potential dosimeters, although pre-sensitization was necessary. A more recent project demonstrated that wallboard may be used as a dosimeter with either EPR or OSL. However, the reduced stability of the dose-sensitive signal with OSL suggests that EPR is the preferred technique. We continue to explore EPR dosimetry of wallboard, and have plans to reproduce earlier promising results of EPR dosimetry with textiles.

6. References

[1] L. Bøtter-Jensen, S. W. S. McKeever, and A. G. Wintle, Optically stimulated luminescence dosimetry, Elsevier Science B.V., London, 2003.

[2] K. Shiraishi, W. Wanitsuksombut, K. Chinudomsub, G. Suzuki, and K. Nishizawa, "ESR dose estimation of the radiological accident in Samut Prakarn, Thailand using sugar samples and an ESR method", *Advances in ESR Applications*, Vol. 18, 2002, pp. 207-209.

[3] A. M. Rossi, C. C. Wafcheck, E. F. de Jesus, and F. Pelegrini, "Electron spin resonance dosimetry of teeth of Goiânia radiation accident victims", *Applied Radiation and Isotopes*, Vol. 52, 2000, pp. 1297-1303.

[4] T. Hashimoto, D. G. Hong, and M. Takano, "Retrospective dosimetry at JCO using luminescence from ceramics pieces and quartz grains", *Advances in ESR Applications*, Vol. 18, 2002, pp. 197-202.

[5] K. Shiraishi, M. Iwasaki, C. Miyazawa, H. Yonehara, and M. Matsumoto, "ESR dosimetry in the JCO criticality accident", *Advances in ESR Applications*, Vol. 18, 2002, pp. 203-206.

[6] International Atomic Energy Agency, "Use of electron paramagnetic resonance dosimetry with tooth enamel for retrospective dose assessment", IAEA, 2002.

[7] W. Gordy, W. Ard, and H. Shields, "Microwave spectroscopy of biological substances. I. Paramagnetic resonance in X-irradiated amino acids and proteins", *Proceedings of the National Academy of Sciences of the United States of America*, Vol. 41, 1955, pp. 983-996.

[8] W. Gordy, W. B. Ard, and H. Shields, "Microwave spectroscopy of biological substances. II. Paramagnetic resonance in x-irradiated carboxylic and hydroxy acids", *Proceedings of the National Academy of Sciences of the United States of America*, Vol. 41, 1955, pp. 996-1004.

[9] D. F. Regulla, "ESR spectrometery: A future-oriented tool for dosimetry and dating", *Applied Radiation and Isotopes*, Vol. 62, 2005, pp. 117-127.

[10] J. A. Weil, J. R. Bolton, and J. E. Wertz, Electron paramagnetic resonance: Elementary theory and practical applications, John Wiley& Sons, Inc., New York, 1994.

[11] V. V. Rudko, I. P. Vorona, N. P. Baran, and S. S. Ishchenko, "γ- and UV-induced CO_2^- radicals in tooth enamel", *Radiation Measurements*, Vol. 42, 2007, pp. 1181-1184.

[12] R. F. H. Khan, "Electron paramagnetic resonance biophysical radiation dosimetry with tooth enamel", Ph.D. thesis, McMaster University, 2003.

[13] R. F. H. Khan, W. J. Rink, and D. R. Boreham, "Dosimetric response evaluation of tooth enamel for accelerator-based neutron radiation", *Radiation Measurements*, Vol. 37, 2003, pp. 355-363.

[14] R. F. H. Khan, W. J. Rink, and D. R. Boreham, "Biophysical dose measurement using electron paramagnetic resonance in rodent teeth", *Applied Radiation and Isotopes*, Vol. 59, 2003, pp. 189-196.

[15] R. F. H. Khan, J. Pekar, W. J. Rink, and D. R. Boreham, "Retrospective radiation dosimetry using electron paramagnetic resonance in canine dental enamel", *Applied Radiation and Isotopes*, Vol. 62, 2005, pp. 173-179.

[16] E. H. Haskell, R. B. Hayes, and G. H. Kenner, "Plasterboard as an emergency EPR dosimeter", *Health Physics*, Vol. 71, 1996, pp. 95.

[17] J. W. Thompson, I. Abu Atiya, W. J. Rink, and D. Boreham, "Potential use of wallboard (drywall) for EPR retrospective dosimetry", *Radiation Measurements*, Vol. 44, 2009, pp. 243-248.

[18] J. Thompson and H. P. Schwarcz, "Electron spin resonance dosimetry and dating potential of whewellite (calcium oxalate monohydrate)", Radiation Measurements, Vol. 43, 2008, pp. 1219-1225.

[19] J. J. Liberda, "Development of a dual purpose synthetic quartz oscillator/emergency dosimeter", M.Sc. thesis, McMaster University, 2008.

[20] J. W. Thompson, K. E. Burdette, E. L. Inrig, R. DeWitt, R. Mistry, W. J. Rink, and D. R. Boreham, "Optically-stimulated luminescence dosimetry with gypsum wallboard (drywall)", *Radiation Protection Dosimetry*, submitted.

[21] C. Larsson, V. Koslowsky, H. Gao, S. Khanna, and D. Estan, "Optically stimulated luminescence in forensics", *Applied Radiation and Isotopes*, Vol. 63, 2005, pp. 689-695.

[22] J. W. Thompson, "Accuracy, precision, and irradiation time for Monte Carlo simulations of single aliquot regeneration (SAR) optically stimulated luminescence (OSL) dosimetry measurements", *Radiation Measurements*, Vol. 42, 2007, pp. 1637-1646.

[23] R. Venkataramani, S. K. Mehta, M. R. Iyer, V. Natarajan, and M. D. Sastry, "Dose determination by ESR in an accident, using cotton fabric", *Journal of Radioanalytical and Nuclear Chemistry, Letters*, Vol. 175, 1993, pp. 17-24.

[24] J. Barthe, V. Kamenopoulou, B. Cattoire, and G. Portal, "Dose evaluation from textile fibers: A post-determination of initial ESR signal", *Applied Radiation and Isotopes*, Vol. 40, 1989, pp. 1029-1033.

[25] V. Kamenopoulou, B. Catoire, and J. Barthe, "Résonance paramagnétique électronique des fibres textiles (coton et polypropylène): application à la dosimétrie d'un accident d'irradiation gamma", *Radioprotection*, Vol. 23, 1988, pp. 277-289.

[26] V. Kamenopoulou, J. Barthe, C. Hickman, and G. Portal, "Accidental gamma irradiation dosimetry using clothing", *Radiation Protection Dosimetry*, Vol. 17, 1986, pp. 185-188.