NEW METHOD FOR ESTIMATING GAMMA-RAY EXPOSURE SUSTAINED IN RADIATION ACCIDENTS
POSSIBILITIES OF USING ORGANIC SUBSTANCES AS MONITOR

TOSHIYUKI NAKAJIMA and SHIGUEO WATANABE

PUBLICAÇÃO IEA N.º 390
Abril — 1975

INSTITUTO DE ENERGIA ATÔMICA
Caixa Postal 11049 (Pinheiros)
CIDADE UNIVERSITÁRIA "ARMANDO DE SALLES OLIVEIRA"
SÃO PAULO — BRASIL

Toshiyuki Nakajima and Shigueo Watanabe

Coordenadoria de Ciência e Tecnologia de Materiais
Instituto de Energia Atômica
São Paulo - Brasil

Publicação IEA Nº 390
Abril - 1975

*Publicado no *Journal of Nuclear Science and Technology*, 11(12):575-82, Dec. 1974

Instituto de Energia Atômica

Conselho Superior

Engº Roberto N. Jafet - Presidente
Prof. Dr. Emilio Mattar - Vice-Presidente
Prof. Dr. Jose Augusto Martins
Prof. Dr. Milton Campos
Engº Helcio Modesto da Costa

Superintendente

Prof. Dr. Rômulo Ribeiro Pieroni

ABSTRACT

A new method is proposed for estimating the amount of exposure to γ-rays sustained by victims involved in a radiation accident. The concept is to use as measure of exposure the quantity of free radicals generated in organic materials by irradiation, and to determine this quantity through its relation to the electron spin resonance shown by substance containing such radicals. Applying this method, a minimum exposure of about 100 R could be estimated with measurements at room temperature. The monitor substances taken up for the present series of experiments included nails and hair taken from exposed persons, plastic button, polyethylene powder, lucite, paper and wool. The experiments were aimed at determining the sensitivity, the fading with lapse of storage time after irradiation and the effects of differences in conditions of storage such as temperature, illumination, and washing before measurement. The method thus developed should prove useful for estimating the extent of exposure, to serve in deciding the medical treatment to be applied.

I. Introduction

A number of accidental exposures have occurred in the past in various countries. Notable examples of such accidents suffered by persons regularly occupied in work involving radiation (referred to hereafter as "radiation-workers", as opposed to "non-workers") include the incidents that occurred at Oak Ridge, U.S.A.[1] and in Yugoslavia[2] (these two cases involving exposure to both neutrons and γ-rays) and in Australia[3] (γ-rays alone). Much effort has been applied to the development of medical treatments to be applied to patients to victims of exposure to radiation.

In the case of accidents suffered by radiation-workers, exposure sustained by them can be estimated more easily and rapidly than in the case of non-workers, since they are constantly subjected to systematic monitoring and control. Nevertheless, the personnel monitors currently used for this purpose are not adapted to convenient and reliable estimation of exposures exceeding 100 R, with the exception of thermoluminescence and glass dosimeters.

For non-workers exposed to γ-rays, no efficacious method of measurement has so far been developed, except the thermoluminescence dosimeter. The present study aims at filling the need felt for a practical and reliable means of gathering information to serve in the treatment of victims of accidental exposure to radiation.

Two approaches — biological and physical — are available for estimating the exposure or absorbed dose sustained by patients upon accidental exposure to γ-rays. Brown & McNeil[3] have reported on a biological method for estimating the absorbed dose. One of the merits of this method is that it permits direct estimation of the dose absorbed by the individual. The method possesses, on the other hand, the intrinsic disadvantage of incurring fairly large

individual factors differing from person to person.

In Japan, there occurred in 1971 an accident involving the exposure of non-workers to γ-rays, on which occasion the present authors established a method for estimating the exposure received by the patients from measurements of the thermoluminescence emitted by jewels taken from wrist watches worn by the patients[4]. This method has the advantage of high sensitivity, but is on the other hand inevitably handicapped by the inherent limitations in the quantity of sample available, and by the impossibility of repeating the measurements. Also, one cannot of course count upon people unexpectedly encountering exposure to be wearing a watch at the time of the eventuality.

In view of these shortcoming of the previously devised method, the authors undertook a study to assemble information that should contribute to the development of a new method for estimating γ-ray exposure, applicable to both radiation-workers and non-workers.

In the present paper, the authors will expose the basic concepts of the new method which utilizes the electron spin resonance of substances containing free radicals.

II. Basic Concept and Measuring Technique

In discussing electron spin resonance, the first item of interest is the Zeeman effect. This takes the form

$$\mathcal{H} = g\beta \mathrm{H} \,.\, \mathrm{S} \tag{1}$$

where $\mathcal{H}$ is the Hamiltonian, β the Bohr magneton, H the applied magnetic field, g the spectroscopic splitting factor and S is the electron spin. The magnetic field is related to the frequency ν of the resonance of free electrons or of free radicals by the expression

$$h\nu = g\beta \mathrm{H}. \tag{2}$$

We next consider the relation between the electron spin resonance and the quantity present of free radicals. It is known that the observable resonance intensity A of a substance is proportional to

$$A = cX'' \tag{3}$$

where c is a constant and X'' the imaginary part of the susceptance of the substance. If the applied magnetic field is fixed, and the frequency of the oscillating magneting field is varied, the intensity A becomes a function of the frequency of which the resonance condition is given by Eq. (2), and is represented by

$$P = \int A(\nu) d\nu, \tag{4}$$

$$P = c\nu_0 \int \frac{X''(\nu)}{\nu} d\nu, \tag{5}$$

In the special case of Kramers-Kronig's relation, we obtain

$$X_0 = \frac{2}{\pi} \cdot \int \frac{X''(\nu)}{\nu} d\nu \tag{6}$$

where X_0 is the susceptance of the sample. Then, it is possible to apply Curie's law to the sample:

$$X_0 = Ng^2 S(S+1)\beta^2 / 3kT \tag{7}$$

Then, the relation between the number N of free electrons or of free radicals and the absorption intensity P becomes

$$P \propto (N/T) g^2 S(S+1). \tag{8}$$

Hence it should be possible to determine the number or quantity of radicals contained in a substance from the absorption intensity of electron spin resonance shown by the substance. Thus, if we can relate the quantity of radicals to irradiation, we see the possibility of estimating the exposure or dose received by a substance from its electron spin resonance intensity.

Now, it is known that when an organic material is exposed to ionizing radiation, free radicals are created therein.

We therefore undertook to determine the quantity of free radicals found after irradiation in such organic substance as polyethylene powder, lucite, ordinary plastic button, paper, wool, cloth of cotton and of polyester, human hair and nail. All the samples, except the hair and nail, were unused materials freshly purchased. Prior to irradiation, the ESR (electron spin resonance) absorption was measured on the samples to determine their natural absorption properties at room temperature. The samples were then irradiated at room temperature with γ-rays from ^{137}Cs source.

The electron spin resonance spectrometer used in this experiment is a JEOL model JES-ME-3X equipped with a 100 kHz modulation unit. The resonance cavity employed operates on the TE_{011} mode, and has a slotted window at one end to permit direct illumination of the sample. The resonant frequency of the loaded cavity was in the range of 9,200 ~ 9,600 MHz. The ESR measurements were made at room temperature.

III. Experimental Results

1. Response of ESR Absorption

In the development of a monitoring method for application to radiation-workers and non-workers, the most important properties of the substance to serve as monitor are its sensitivity and fading behavior.

Figure 1 reveals the linear relationship obtained between the exposure to ^{137}Cs γ-rays and the ESR absorption intensity of polyethylene powder irradiated in the dark.

The vertical axis is the relative ESR absorption intensity due to the free radicals in the sample irradiated with γ-rays, observed at room temperature within 2 hr after irradiation. The intensity was normalized in respect of both the weight of the sample and the intensity of the standard sample of DPPH.

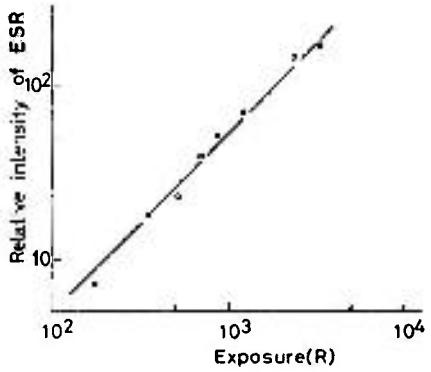


Fig. 1

Relative ESR absorption intensity *vs.* γ-ray exposure shown in polyethylene

It seen from Fig. 1 that good linearity was obtained between the ESR absorption intensity and the exposure, in the entire range of 180 ~ 5,000 R. While it is desirable that a monitor for use in radiation accidents should be capable of measuring a minimum exposure of about 10 R, it proved that under the present conditions, the ESR method should only be able to estimate exposures down to 100 R, below which the ESR signal level would be too low. It is however to be noted in Eq. (8) that the ESR absorption intensity is inversely proportional to the measuring temperature. It follows from this that if the ESR absorption can be measured at either liquid nitrogen or liquid helium temperature, an exposure of about or even 1 R could be estimated by the proposed ESR technique. The method would then acquire the desired sensitivity for radiation accident monitoring. Measurements made during the present work, on polyethylene, plastic button, lucite, wool and cotton cloth showed that the sensitivities of all these substances were roughly similar to each other.

2. Fading

The precise timing of an accidental exposure to radiation is inherently difficult to determine precisely. Thus it becomes important to minimize fading or decay of the free radicals generated by irradiation in the substances to utilize as monitor, between the time of their exposure and their measurement. It should of course be ideal to use substances that show no

radicals.

The fading properties under different conditions of storage were examined on samples of plastic button, polyethylene and lucite, all irradiated at room temperature with γ-rays. An example of the results of measurements on fading in the sense given above is shown in **Fig. 2**, where the curve represents the fading of the free radicals in polyethylene, kept in the dark at room temperature after irradiation to 10^3 R. It is seen from Fig. 2 that the free radicals gradually decreased, dropping in 2 days to about 88% of the initial ESR absorption intensity. Even so, the decay shown by polyethylene was less prominent than in the case of other organic materials such as lucite, button and human hair.

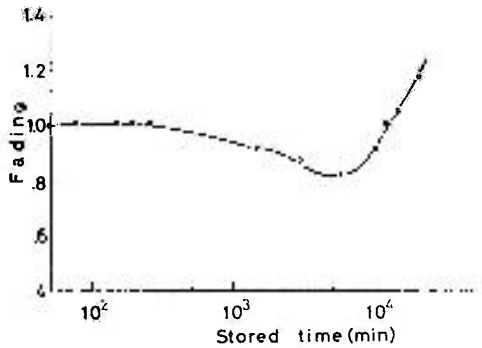


Fig. 2
Fading of free radicals in irradiated polyethylene stored at room temperature

The decay observed in the case of wool and human hair and nail was very rapid, and for example, in human hair the ESR absorption intensity was reduced by one half between the first and the second observations, separated by a lapse of 5 min. These substances are therefore not suitable for monitoring.

3. Effect of Differences in Storing Temperature on Decay of Free Radicals

Figure 3 shows how the change brought by lapse of time to the ESR absorption intensity of lucite is modified by the temperature at which the sample is stored after irradiation at room temperature. The vertical axis is the ratio between the ESR absorption intensities of samples measured immediately after irradiation and measured after storing for various periods.

It is seen from the figure that, at room temperature, the response gradually decreased with storage time, dropping down to about 90% at 1,300 min after irradiation. When stored at 0°C, the 90% level was only reached at 10,000 min, while at 42°C, the response deteriorated very rapidly. When stored at 100°C (**Fig. 4**), the response of the sample was reduced to 0.01%

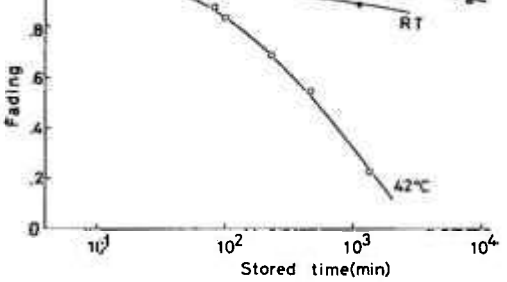


Fig. 3

Fading of free radicals in irradiated lucite stored at various temperatures

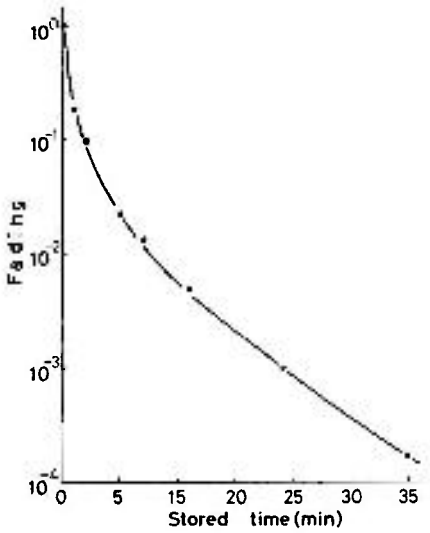


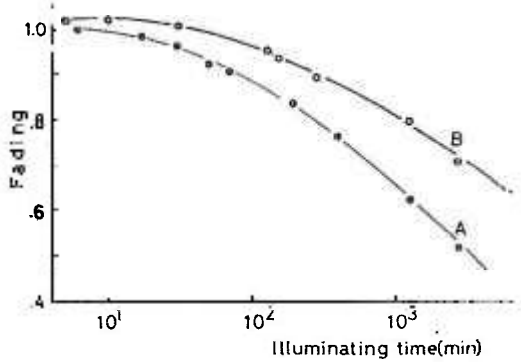
Fig. 4

Fading of free radicals in irradiated lucite stored at 100°C

The mechanism of the decrease of the free radicals at high temperature is not yet understood fully, but it is indicated from the foregoing result that certain organic materials should be utilizable in radiation dosimetry, provided they are stored at room temperature or below after irradiation, while after measurement, storing the sample at high temperature for 30 min or more should restore the substance to a state suitable for re-use or for recalibration.

applied at room temperature.

Figure 5 shows the results obtained with (B) and without (A) illumination at room temperature on irradiated plastic buttons. It is indicated that the samples are sensitive to some extent to illumination, but in practical applications this property could be neglected because of relatively short duration of illumination to which the samples would be subjected to after irradiation. Further, the degree of influence should depend on the wavelength of the light, since it may be considered that the cause of the increase seen in ESR response upon illumination is the generation of additional free radicals by ultra-violet light.

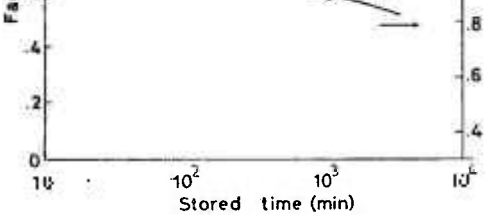


Curve A: without illumination
Curve B: with illumination
Both at room temperature

Fig. 5

Effect of illumination on fading of free radicals in irradiated plastic button

As already mentioned, the free radicals in many organic materials are not stable at room temperature in air. It is well established that the decay of the free radicals is due to their reaction with oxygen contained in the air. Thus, if such a sample is coated with some protective material before irradiation, the decay might be less rapid than in the case of an un-coated sample. **Figure 6** shows the results of a test with carbon paint coating on the lucite to see its effect on the decay of the free radicals in lucite. It is seen that the coating did not bring any beneficial effect. On the other hand, it has been reported that irradiated samples stored in vacuum were preserved free of decay[6]. Then, in case where monitor samples subject to rapid decay of the free radicals contained therein must be stored before measurement, preservation in vacuum may possibly be an effective measure for using them as monitor or dosimeter.



Curve A: un-coated, Curve B: coated

Fig. 6

Effect of carbon coating on fading of free radicals in irradiated lucite stored at room temperature

5. Washing Effect on Decay of Free Radicals

Our aim being to utilize samples of organic materials found on the patients' body and among their personal effects and belongings such as hair, nail, plastic accessories and part of clothing as monitor substance for the estimation of exposure in a radiation accident, it must be expected that the samples made available in actual application would generally be soiled and dirty. Since dirt would become source of noise in the subsequent measurements of ESR absorption, the samples collected from the patients should first have to be cleaned. In view of this circumstance, a study was made of the effect of cleaning on irradiated lucite.

Table 1 gives the effect of various solvents on the decay of free radicals in the lucite.

Table 1

Effects on decay of free radicals shown by some solvents for dirt and soil

Alcohol	Aceton	Benzen	Shap and water	Water	Mineral oil
0.995 ±0.0042	0.993 ±0.0428	0.996 ±0.0023	0.996 ±0.0030	1.00 ±0.001	0.972 ±0.0026

The irradiated samples were washed for 5 min at room temperature with each solvent. The results given in Table 1, indicate that water and organic solvents scarcely affect the decay of the free radicals, while mineral oil is seen to have a distinct influence. Differences in the duration of washing, as seen in Fig.7, produced no consistent effect, within the range covered, from 0,5 to 21 min. In the experiment shown Fig. 7, the irradiated lucite was washed with benzene. The foregoing results would indicate the utility of washing soiled samples with water

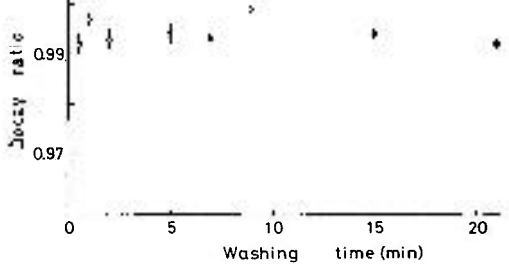


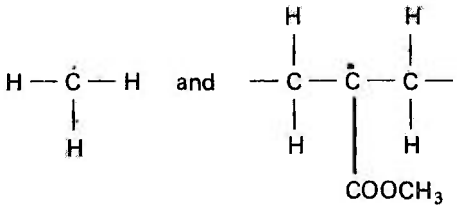
Fig. 7

Decay of free radicals in irradiated lucite by washing with benzene

6. Application to Dating of Accident

The main purpose of the present study was to estimate the exposure or the absorbed dose. But if a monitor could further estimate also the period elapsed since the accidental irradiation, this would add to the utility of the monitor. It has been seen in the preceding sections that, after irradiation of organic substance, the free radicals produced decay inevitably to some extent with lapse of time. The rate at which this decay proceeds would of course be expcted to differ according to type of the free radical.

Figure 8 shows the ESR spectrum of lucite irradiated at room temperature with γ-rays from ^{137}Cs source. Analysis of this spectrum indicates the presence of two kinds of free radical



Thus, if one of the free radicals in the sample has faded markedly, and the other only very little, the ratio between the ESR absorption intensities due to the two different radicals could be a function of the time elapsed after the exposure. And if this is true, the ratio could be measured to give an estimation of the timing of the exposure.

To ascertain this possibility, experiments were perfomed with lucite and with polyethylene powder sample containing a few free radicals.

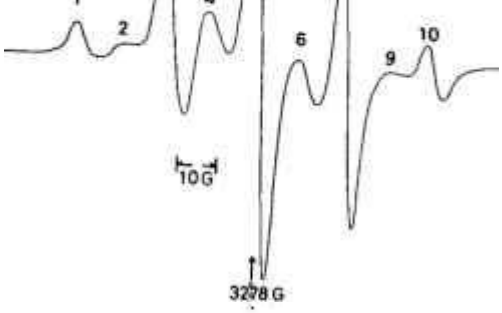


Fig. 8

ESR spectrum of irradiated lucite observed at room temperature

Figure 9 shows the result obtained with polyethylene, and reveals the changes observed in the ratio of ESR absorption intensities between at the position of the free electrons and at that of other radicals in the vicinity of the position occupied by the free electrons, as a function of time after exposure. This ratio is independent of both extent of exposure and energy of radiation. These results confirm the possibility of estimating the dating of the accidental exposure through ESR measurements.

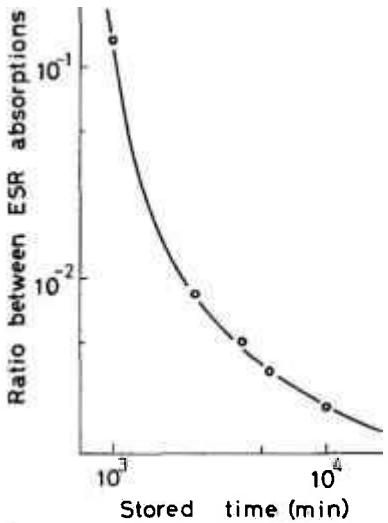


Fig. 9

Changes in time of ratio between ESR absorption peak due to free electrons and that due to other free radicals — polyethylene stored at room temperature

In this experiment, we have undertaken to obtain some information that could contribute to the development of a method for estimating the exposure or the absorbed dose received by radiation-workers and non-workers in a radiation accident. It is proposed to utilize measurements of the electron spin resonance of the free radicals generated by irradiation in organic materials. We shall here consider the differences between the present and other current methods.

Since non-workers cannot be expected to be carrying personnel monitors at the time of an accidental exposure to radiation, the exposure data required for the ensuring medical treatment must be sought either among their personal belongings or in their own body. We have previously developed a thermoluminescence method utilizing jewels in the wrist watch as monitor substance[4]. The drawbacks of this method are as mentioned above in the "Introduction".

The ESR method, proposed with the aim of covering the shortcomings of the watch-jewel method, possesses, in turn, the inherent drawback of poor sensitivity compared with the normally used dosimeters such as film badge, pocket chamber, glass dosimeter and thermoluminescence dosimeter. It is, however, to be noted that radiological information can already be of use to doctors treating patients involved in a radiation accident, even if can only distinguish and classify the dose received into the very rough ranges of (a) below 100 rad, (b) between 100 and 300 rad, and (c) above 300 rad. This order of precision should be well within the scope practical realization with the proposed approach based on ESR measurements, considering the large quantity and choice of monitor substance available for this method.

Another useful property to be borne in mind is that the ESR absorption intensity is proportional to the reciprocal of the measuring temperature, as indicated by Eq. (8). Thus the sensitivity of the method should be markedly improved by performing the ESR measurements at very low temperatures. While it may not be practical to attempt such measurements at liquid helium temperature, that of liquid nitrogen should be relatively easy. And the present experimental results would indicate that it should be quite possible to detect exposures of about 10 rad at liquid nitrogen temperature, which should fully qualify the proposed method as means of obtaining exposure information of use in medical treatment.

The expense involved in equipment for ESR measurements is offset by the ease with which the monitor substances could be collected from the personal effects of the patients. This abundant availability of monitor substance is the strongest advantage of the proposed method, and in this respect it is the converse of the method utilizing the thermoluminescence of watch jewels reported in the previous paper[4].

V. Conclusion

We have examined the possibilities of utilizing the electron spin resonance absorption

involved in accidental exposure to radiation.

(2) If the monitoring is effected within 1 week after the accident, it should be quite possible to estimate the exposure, before effacement by fading of the effects of radiation sustained by the monitors substances.

(3) Illumination of irradiated monitor sample was found to increase rather than decay the free radicals, but only by a small amount.

(4) Heat distinctly accelerated the decay of free radicals in the irradiated monitor sample. It is hence desirable that the monitor substance be maintained at a temperature as low as possible during the period between exposure and measurement.

(5) There is possibility of dating the time of exposure by this method.

Effects similar to those observed in the present experiment should be found also in the case of other kinds of the organic material. Thus we have a large choice of monitor substances to select among the organic materials around exposed persons, on which to apply the proposed method of radiation dosimetry for accidental exposure to radiation.

The authors intend to follow the present study with the development of a practical dosimeter based on the principles described above.

Acknowledgment

The authors wish to express their thanks to Prof. R. R. Pieroni, Director of the Institute of Atomic Energy, São Paulo, for his encouragement of the work, which was supported by grants from CNEN and FAPESP in Brazil.

RESUMO

Foi aqui proposto um método novo para fazer a estimativa da exposição de raios gama a que vítimas foram sujeitos num acidente de radiação. A idéia consiste em usar como medida de exposição a quantidade de radicais livres produzidos em materiais orgânicos por irradiação, e determinar esta quantidade pela medida da ressonância paramagnética eletrônica. Aplicando este método, uma exposição mínima de cerca de 100 R pode ser determinada com medidas em temperatura ambiente. As substâncias monitoras usadas na presente série de experiências são unhas e cabelos de pessoas expostas, botão plástico, pó polietileno, lucite, pepel e lã. As experiências foram destinadas à determinação de sensibilidade do desvanecimento com o tempo de armazenamento após a irradiação e dos efeitos das diferenças nas condições de armazenamento, tais como a temperatura, iluminação e lavagem antes da medida. O método assim desenvolvido será útil na estimativa do grau da exposição para auxiliar na decisão do tratamento médico a ser aplicado.

RÉSUMÉ

Une nouvelle méthode d'evaluation de l'exposition de rayonnements gamma à lesquels des victimes ont été assujetis dans un accident de radiation. L'idée consiste d'utiliser comme la mésure d'exposition la quantité des radicaux libres crées dans les matériaux organiques pour irradiation, et déterminer cette quantité pour la mésure de la resonance paramagnétique éléctronique. Pour l'application de cette méthode, une exposition minimum d'environ 100 R péut être déterminée avec les mésures à la temperature ambiante. Les substances

moniteures utilisées dans cette série d'expériences sont les ongles, les cheveux des personnes exposées, le boutton plastique, poudre polietilène, lucite, papier et laine. Les expériences sont destinées à la détermination de la sensibilité, de la dissipation au cours du temps de la magasinage aprés l'irradiation, et.des effects des differences dans les conditions de la magasinage, comme la temperature, l'illumination et la lavage avant de la mésure. La méthode ici developée, sera utile pour l'evaluation du degré d'exposition pour aider la decision du traitement médical pour être appliqué.

REFERENCES

1. ABE, E. Unkown title. *Solid State Physics*, of Japan, (7):129, 1958.

2. ANDREWS, G. A. et alii. The importance of dosimetry to the medical management of persons accidentally exposed to high levels of radiation. In: INTERNATIONAL ATOMIC ENERGY AGENCY, Vienna. *Personal dosimetry for radiation accidents: proceedings of a symposium on . . . held in Vienna, 8-12 March 1965.* Vienna, 1965. p.3-16.

3. BROWN, J. K. & McNeil, J. R. Biological dosimetry in an industrial radiography accident. *Hlth Phys.*, New York, **21**:519-22, 1971.

4. CALLIHAN, D. & THOMAS, J. T. Accidental radiation excursion at the Oak Ridge Y-12 Plant - I: description and physics of the accident. *Hlth Phys.*, New York, **1**:363-72, 1959.

5. MILLER, A. A. Radiation chemistry of polyvinyl chloride. *J. phys. Chem.*, Ithaca, N. Y., **63**:1755-9, 1959.

6. NAKAJIMA, T. et alii. New gamma-ray exposure estimation method for radiation accident. *J. Nucl. Sci. Technol.*, Tokyo, **10**(4):202-6, 1973.