

## DEVELOPMENT AND CURRENT STATE OF DOSIMETRY IN CUBA

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**Abstract**

In Cuba, the application of the radiation technologies has been growing in the last years, and at present there are several dosimetry systems with different ranges of absorbed dose. Diverse researches were carried out on high dose dosimetry with the following dosimetry systems: Fricke, ceric-cerous sulfate, ethanol-chlorobenzene, cupric sulfate and Perspex (Red 4034 AE and Clear HX). In this paper the development achieved during the last 15 years in the high dose dosimetry for radiation processing in Cuba is presented, as well as, the current state of different dosimetry systems employed for standardization and for process control. The paper also reports the results of dosimetry intercomparison studies that were performed with the Ezeiza Atomic Center of Argentine and the International Dose Assurance Service (IDAS) of IAEA.

## 1. INTRODUCTION

As part of the Cuban nuclear programme and the applications of the nuclear techniques, particularly the employment of the gamma sources in radiation processing, a number of studies have been realized and different dosimetry systems applied which insure the radiation processing quality.

At present, Cuba has two laboratory irradiators located in the Center of Applied Studies for Nuclear Development, and a laboratory irradiator in the Laboratory for Irradiation Techniques. Cuba also has a semi-industrial irradiation plant belonging to the Research Institute for Food Industry, in which different applications have been developed in the field of radiation processing, such as food preservation, sterilization of medical and pharmaceutical products, treatment of biological products, radiobiology and treatment of polymers. To obtain the desired technological effect, it is necessary to know the absorbed dose value by means of accurate and reliable dosimetry systems employed during the commissioning of the facility, during process qualification and for process control, and also to have appropriate documented procedures.

The present paper describes the studies carried out for different dosimetry systems employed in high dose dosimetry in Cuba, as well as the results obtained in the dose intercomparison exercises.

## 2. FRICKE DOSIMETRY SYSTEM

In radiation processing, Fricke is a generally accepted reference standard dosimeter for in-house absorbed dose calibration. We have employed this dosimeter for calibration of other dosimetry systems, for process control and commissioning of different irradiators in our country.

The influence of different factors on the molar extinction coefficient value was studied, as well as, the effect of the measurement wavelength, the oxygen concentration in the dosimetric solution and the measurement equipment to obtain a good precision and accuracy in the absorbed dose value with this dosimeter [1,2].

## 2.1. Molar extinction coefficient ( $\epsilon$ )

The molar extinction coefficient value of any system generally depends on several factors, such as the preparation procedure, quality of the ingredients, dissolvent, wavelength and temperature. We found that for a set preparation procedure [3], the temperature, measurement wavelength and the quantity of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in the solution were the most influential factors.

A factorial plan  $2^3$  was followed in which the above factors were taken into account at two measurement levels as independent variables (see Table I).

TABLE I. MEASUREMENT LEVELS OF THE INDEPENDENT VARIABLES.

	Low level	High level
Temperature ( $^{\circ}\text{C}$ )	24	25
Wavelength (nm)	303	305
$\text{H}_2\text{O}_2$ quantity (mL)	4	10

The experimental results showed that the measurement temperature and the quantity of hydrogen peroxide in the solution had significant influence on the  $\epsilon$  value, whereas the wavelength and the interaction of the tested parameters do not have significant effect. Thus, the mathematical model is given by:

$$y = 219.4 + 1.0 \left\{ (T - 24.5) / 0.5 \right\} - 1.6 \left\{ (\text{H}_2\text{O}_2 - 7) / 3 \right\}$$

Substituting different values of temperature and hydrogen peroxide in this expression, the calculated  $\epsilon$  value is in the range of 216.8 – 222.0 ( $\text{m}^2 \cdot \text{mol}^{-1}$ ). The results agree with the values reported in the literature [4,5].

This model is appropriate for this range of the variables and for our spectrophotometer, as the  $\epsilon$  value is different for each spectrophotometer.

## 2.2. Measurement wavelength

The ferric ion concentrations were determined at 224 and 304 nm in the spectrophotometer, Busch & Lomb Spectronic 1001 type, for seven different radiation times to determine the influence of the measurement wavelength on the absorbed dose value.

Table II shows the absorbed dose values obtained for the two wavelength values. A linear regression analysis is made in which it is obtained for the measurement at 224 nm a functional relation of  $D(\text{Gy}) = 10.07 + 11.36 t(\text{min})$ , and the correlation coefficient value ( $r$ ) of 0.9997, and for 304 nm the relation is  $D(\text{Gy}) = 9.18 + 11.55 t(\text{min})$  and  $r = 0.9998$ . Finally a Duncan test was made and it was determined that there is no significant difference between these two expressions. It shows that it is not necessary to make the measurements at 224 nm when the equipment of high precision and a control of measurement temperature are used, although the temperature coefficient for 224 nm is only 0.13 %  $^{\circ}\text{C}^{-1}$  between 20 and 30  $^{\circ}\text{C}$ , in comparison with 0.7 %  $^{\circ}\text{C}^{-1}$  at 304 nm [6].

TABLE II. ABSORBED DOSE VALUES (Gy) AND THE STANDARD DEVIATIONS FOR WAVELENGTH ( $\lambda$ ) OF 224 AND 304 nm

Radiation time (min)	$\lambda=224$ nm	$\lambda=304$ nm
1.4	26.10 $\pm$ 3.68	24.62 $\pm$ 3.36
2.8	40.24 $\pm$ 1.36	38.62 $\pm$ 1.29
7.05	92.61 $\pm$ 2.51	93.15 $\pm$ 2.60
14.11	167.74 $\pm$ 5.36	170.56 $\pm$ 5.17
21.21	254.61 $\pm$ 11.23	260.04 $\pm$ 11.27
28.26	329.43 $\pm$ 11.02	336.65 $\pm$ 11.52
35.60	404.50 $\pm$ 16.75	417.07 $\pm$ 19.66

### 2.3. Oxygen concentration in the dosimetric solution

The ferric ion concentrations of the un-saturated and saturated solutions with oxygen were determined at 304 nm in a spectrophotometer, type Sf-4, for five different irradiation times. The absorbed dose values are given in Table III, as well as, the standard deviations for each irradiation time for the two Fricke solutions. The data show that the relation between the absorbed dose and the irradiation time is linear for both solutions; the expressions are  $D(\text{Gy})=9.68+11.59 t(\text{min})$ ,  $r=0.9989$  and  $D(\text{Gy})=9.71+11.52 t(\text{min})$ ,  $r=0.9998$ , respectively.

TABLE III. ABSORBED DOSE VALUES (Gy) AND THE STANDARD DEVIATIONS FOR THE UN-SATURATED AND SATURATED FRICKE SOLUTIONS.

Radiation time(min)	Un-saturated O <sub>2</sub> Fricke	Saturated O <sub>2</sub> Fricke
2.80	37.82 $\pm$ 6.31	39.57 $\pm$ 1.42
7.05	90.40 $\pm$ 6.66	92.67 $\pm$ 4.87
14.11	182.25 $\pm$ 9.22	173.75 $\pm$ 6.69
21.21	256.60 $\pm$ 10.24	255.04 $\pm$ 3.93
28.26	332.97 $\pm$ 12.20	333.96 $\pm$ 11.71

A Duncan test was carried out for this exercise also, and it showed that there is no significant difference between the two solutions (un-saturated and saturated). For this reason, it is not necessary to saturate the solution with oxygen in the working range of Fricke dosimeter (40 - 330 Gy).

### 2.4. Measurement equipment

To determine the influence of the measurement equipment on the absorbed dose value, the un-saturated solution was irradiated and the measurements were made with Sf-4 and Bausch & Lomb Spectronic 1001 spectrophotometers, the molar extinction coefficient value of each equipment is 219.6 and 213.8  $\text{m}^2 \cdot \text{mol}^{-1}$ , respectively for the wavelength of 304 nm.

The absorbed dose values obtained for different irradiation times are presented in Table IV. By means of a Duncan test it is determined that there is no significant difference between the results for the dose range studied, although some researchers have reported that there are differences when the measurements are made with different equipment [4,7]; this could be possible when the molar extinction coefficient value is not determined for each spectrophotometer separately.

TABLE IV. ABSORBED DOSE VALUES (Gy) AND THE STANDARD DEVIATIONS FOR DIFFERENT MEASUREMENT EQUIPMENT AT 304 nm.

Radiation time(min)	Sf-4	Bausch &Lomb Spectronic 1001
2.80	37.82 ± 6.31	38.62 ± 1.29
7.05	90.40 ± 6.66	93.15 ± 2.60
14.11	182.25 ± 9.22	170.56 ± 5.17
21.21	256.60 ± 10.24	260.04 ± 11.24
28.26	332.97 ± 12.20	336.65 ± 11.52

### 3. CERIC-CEROUS SULFATE DOSIMETRY SYSTEM

Ceric-cerous sulfate is a reference standard dosimeter which can be used for the measurement of radiation dose in kGy range. It is particularly well suited for the measurements of dose in the range of about 20 to 30 kGy which is the important range for sterilization [8].

This dosimetry system has been studied to understand the influence of: ceric concentration, molar extinction coefficient, dilution factor of the sample and stability of the dosimetric solution before and after irradiation (diluted and un-diluted) [9]. The measurement of the cerous ion concentration is made in Pye Unicam 8600 spectrophotometer at wavelength of 320 nm.

#### 3.1. Influence of ceric concentration

A stock solution was prepared of 100-mM ceric sulfate. From this stock solution were made ceric and ceric-cerous solution of 1.5 mM for the dose range of 0.6-5 kGy, and another one of 10 mM for the dose range of 5-40 kGy; the radiation yield value (G-value) is  $2.32 \times 10^{-7}$  and  $2.26 \times 10^{-7} \text{ mol} \cdot \text{J}^{-1}$ , respectively.

For the 1.5-mM solution, the measured dose rate was 0.036 kGy/min ( $r=0.999$ ) as compared to 0.035 kGy/min ( $r=0.997$ ) determined by Fricke; this represents a relative error of 2.7 %, which agrees with the values reported in other papers [10].

For the 10-mM solution, the measured dose rate was 0.70 kGy/h ( $r=0.999$ ) as compared to 0.715 kGy/h determined by the Fricke dosimeter; this represents a relative error of 2 %. Similarly, for the ceric-cerous solution, the estimated dose rate value was of 0.315 kGy/h while the value with Fricke was 0.318 kGy/h ( $r = 0.999$ ) which represents a relative error of 0.9 %. This demonstrates that with high concentration values of ceric ions the system is more stable.

#### 3.2. Influence of molar extinction coefficient

We have determined the  $\epsilon$  values for the concentrations of 1.5 and 10 mM; these are  $562.2 \pm 4$  and  $564.5 \pm 2 \text{ m}^2 \cdot \text{mol}^{-1}$  respectively. This represents a relative error of 0.6 % for the higher of the two values with relation to the value of  $561.0 \text{ m}^2 \cdot \text{mol}^{-1}$  reported in the literature [11,12].

#### 3.3. Dilution factor

Dilution of unirradiated and irradiated solutions is needed to bring the optical density within the measurement range of the spectrophotometer (0.04-0.2 mM). Dilution factors as high as 250 are reported [12], although we did not obtain good results with these values. By means of a study, dilution factors of 12.5 and 100 for the 1.5 and 10 mM concentrations were determined.

### 3.4. Stability before irradiation

With good preparation, clean glassware and an appropriate storage, the stock ceric solution is stable for six months and the solution of 10-mM concentration is stable for four months, in agreement with the reported values [10,13]. On the other hand, the stock ceric-cerous solution is stable for one year and its dilutions, 1.5 and 10 mM prepared immediately, showed a stability of eight months. Since ceric sulfate solution is sensitive to light, which is more significant at low concentrations, care should be taken to avoid errors in dosimetry by photo-reduction.

### 3.5. Stability after irradiation

Table V shows the variation in the evaluated dose values for the solution diluted immediately after the radiation process and the solution diluted at the time of measurement for different times. In the first case, a relative error of -14.2% could occur if measured after 24 hours, and this error increases with time. However in the second case, the error is less than 10% for one week and this value does not increase as quickly as in the first case. Besides, in the first case the dose value increases, while for the second case the dose value decreases with time.

TABLE V. VARIATION OF ABSORBED DOSE WITH MEASUREMENT TIME.

Measurement time	Solution diluted immediately after irradiation			Solution diluted at the time of measurement		
	Dose(kGy)	Variation coefficient	Relative error(%)	Dose(kGy)	Variation coefficient	Relative error(%)
Immediately	10.893 ± 0.104	0.0096	---	10.960 ± 0.212	0.0193	----
3 hours	11.613 ± 0.291	0.0250	- 6.1	10.746 ± 0.115	0.0107	1.9
24hours	12.696 ± 0.052	0.0041	-14.2	10.672 ± 0.035	0.0032	2.6
1 week	13.102 ± 0.104	0.0079	-16.86	10.084 ± 0.081	0.0080	7.9
2 week	13.357 ± 0.050	0.0037	-18.44	9.272 ± 0.062	0.0066	15.3
3 week	14.978 ± 0.052	0.0034	-27.27	9.274 ± 0.071	0.0076	15.3
4 week	17.002± ---	---	-35.93	8.023 ± 0.047	0.0058	26.7

## 4. ETHANOL-CHLOROBENZENE DOSIMETRY SYSTEM

We use ethanol-chlorobenzene dosimeters for routine control in radiation processing due to the following properties: appropriate accuracy, quick evaluation, dosimeter solution and dosimeters can be easily prepared and stored for a long time, and chemicals are inexpensive [14]. The evaluation of the absorbed dose is made by measuring the electrical conductivity of the irradiated solution in an oscillotitrator equipment, OK-302/2 type, at a frequency of 48 MHz.

The calibration curve was obtained by means of a regression analysis with the following functional dependence:  $D$  (kGy)= $a \cdot x^b$  for 2-40 kGy, and another of  $D$  (kGy)=  $a + b \cdot x$  for 1-2 kGy, where  $a$  and  $b$  are coefficients and  $x$  is the deflection of the needle in the equipment. The dosimeters prepared in our laboratory were intercompared with the dosimeters supplied by the Institute of Isotopes of the Hungarian Academy of Sciences, where a good agreement was found. To study the effect of storage, a few dosimeters were stored for six months in dark at a temperature of  $25 \pm 1$  °C; the maximum variations of  $\pm 10$  % with relation to the value measured immediately after irradiation were found [15].

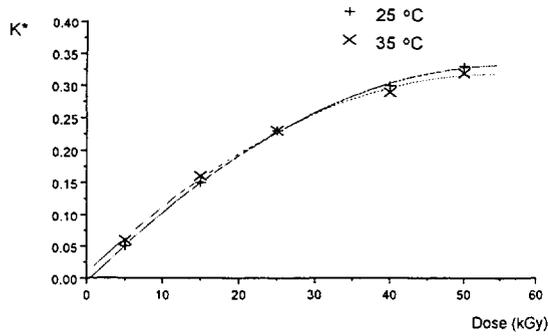


FIG. 1. Calibration curves of the Red Perspex irradiated at 27 °C. Storage temperatures are 25 and 35 °C ( $\lambda = 640$  nm).

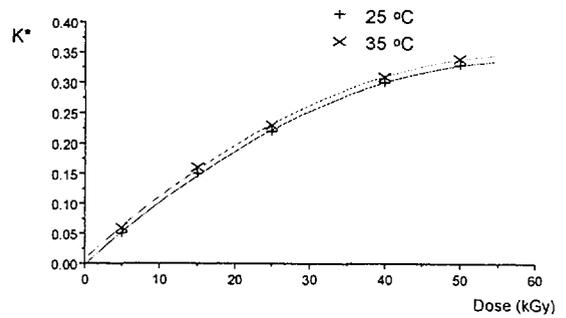


FIG. 2. Calibration curves of the Red Perspex irradiated at 40 °C. Storage temperatures are 25 and 35 °C ( $\lambda = 640$  nm).

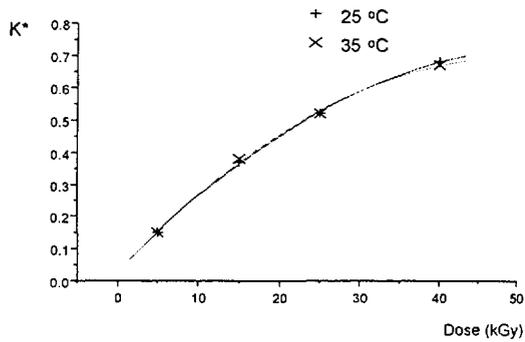


FIG. 3. Calibration curves of the Clear Perspex irradiated at 27 °C. Storage temperatures are 25 and 35 °C ( $\lambda = 315$  nm).

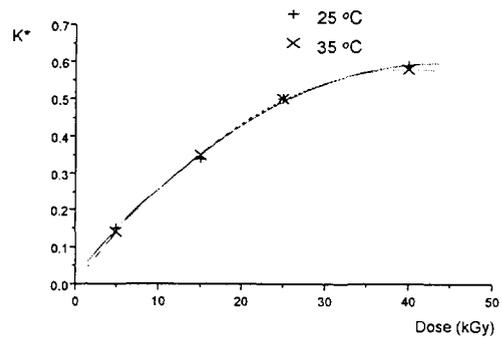


FIG. 4. Calibration curves of the Clear Perspex irradiated at 40 °C. Storage temperatures are 25 and 35 °C ( $\lambda = 315$  nm).

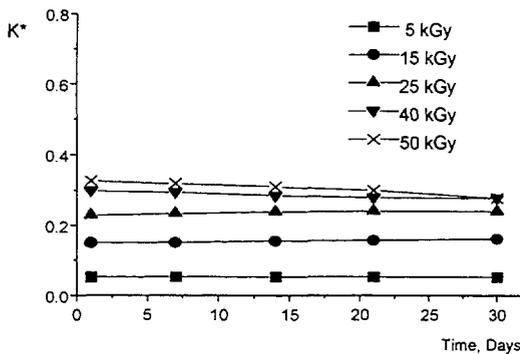


FIG. 5. Post-irradiation  $K^*$  variations for different absorbed dose values for the Red Perspex irradiated at 27 °C and stored at 25 °C ( $\lambda = 640$  nm).

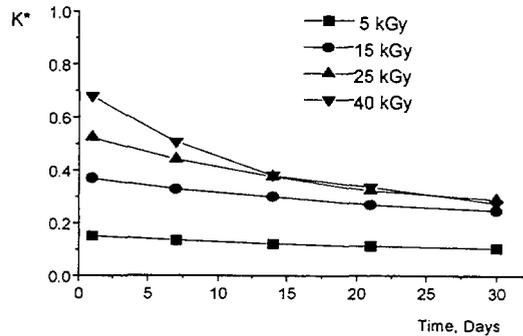


FIG. 6. Post-irradiation  $K^*$  variations for different absorbed dose values for the Clear Perspex irradiated at 27 °C and stored at 25 °C ( $\lambda = 315$  nm).

## 5. CUPRIC SULFATE DOSIMETRY SYSTEM

Cupric sulfate dosimeters have been employed for radiation process control of several products, but much less often compared to other dosimeters because of the instability of the dosimetric solution. For this reason, it is necessary to employ fresh solution for each irradiation [16]. The dosimeter was calibrated, using the Pye Unicam 8600 spectrophotometer and analysis wavelength of 305 nm, in the dose range of 1-8 kGy, where the following functional relation was obtained:

$D(\text{kGy}) = 0.27 + 0.64 t(\text{min})$ ,  $r=0.997$ , as well as good results for radiation process control.

## 6. PERSPEX DOSIMETERS (RED 4034 AE AND CLEAR HX)

The Perspex dosimeters are inexpensive, tissue equivalent, accurate and easy to handle, that can be used for industrial applications such as radiation sterilization of medical products and food irradiation [17].

The red Perspex dosimeters were irradiated for the dose range 5 – 50 kGy and the absorbance change was measured at 640 nm wavelength, while the clear Perspex dosimeters were irradiated between 5 – 40 kGy and the absorbance was measured at 315 nm. The irradiations were carried out at  $27 \pm 1$  and  $40 \pm 1$  °C. After irradiation, the dosimeters were stored at two temperature values (25 and 35 °C) [18]. Figures 1 and 2 show, for the red Perspex dosimeters, the relationship between the induced specific absorbance value ( $K^*$ ) and absorbed dose for irradiation temperature of 27 and 40 °C and different storage temperatures (25 and 35 °C), where it is observed that the behaviour is different. On the other hand, the results obtained with the clear Perspex HX (Batch No.7) dosimeters, as shown in Figs 3 and 4, show similar behavior for the two storage temperatures up to about 30 kGy; there is some influence of the storage temperature for higher dose values.

In Fig. 5, the variation of  $K^*$  is presented for red Perspex dosimeter with relation to post-irradiation time for different absorbed dose values. It shows that  $K^*$  decreases significantly for high dose values with time. However, for doses below 25 kGy,  $K^*$  is reasonably stable over 30 days. The behavior of the clear Perspex dosimeters is shown in the Fig. 6, where the  $K^*$  value decreases with time for all dose values investigated. This places a very severe restriction on the use of this dosimeter.

## 7. QUALITY ASSURANCE PROGRAMME

We have developed a Dosimetry Good Practice Manual which constitutes the first step for a Quality Assurance Program. This manual has the following aspects: dosimetry procedures, equipment control, laboratory techniques manual and reported results. It is very important for process control for our irradiation facility.

## 8. DOSE INTERCOMPARISON EXERCISES

We had participated in two dose intercomparison exercises in 1996, where ceric-cerous sulfate dosimeters were employed. One exercise was carried out at three different dose values in the range of 10-50 kGy with the Dosimetry Laboratory for Radiation Processing of Ezeiza Atomic Center, Argentina. They employed their silver/potassium dichromate dosimeters for this exercise. The minimum relative error between the two dosimetry systems was 4.4 % and the maximum error was 5.8%. The other intercomparison exercise was with the International Dose Assurance Service (IDAS) of the IAEA for two dose values using alanine dosimeter, where the relative errors were -1.77 and -2.85 %. This indicates that our dosimetry system is suitable and accurate for the measurement of medium and high doses.

## 9. CONCLUSION

The gained experience has allowed us during these years of work in Cuba to understand and characterise suitable and accurate dosimetry systems for the radiation process quality control. Also, we have developed appropriate methodologies to improve the available materials. Besides, we have studied the influence of different factors on the behaviour of the dosimeters for our conditions, which allow us to obtain more accuracy in the absorbed dose values.

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