MEASUREMENTS WITH DICARBOXYLIC ACID DOSIMETERS

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General

Three systems were used: aqueous oxalic acid (1,2), solid oxalic acid (3) and solid succinic acid (4) (Table 1). Molecules of these acids decompose under radiation and this change is used for the purpose of dosimetry. The dosimetric reaction follows a first order expression up to about 50% decomposition. The value of the proportionality factor, a, is specific for the system and it depends on the type of radiation. All three systems are sensitive to both gamma and fast neutron radiation. Therefore, they measure the total absorbed energy in a mixed radiation field. They do not become radioactive in a thermal neutron flux and can be handled under normal conditions.

The advantage of these dosimeters is the ease of routine use in known radiation fields (i.e. known contributions of different types of radiation in the mixture).

The measurements in the GRR reactor at the Democritos centre were done at the positions Δ-6 and B-7, 9 cm above the centre line of the fuel elements.

Experimental Procedure and Measured Values

(1) Aqueous oxalic acid

A 250 mM oxalic acid solution was used. About 3 ml of this dosimetric solution were irradiated in a sealed quartz ampoule placed in an Al can. Two irradiations were made at each position.

Oxalic acid concentrations before (c_o) and after (c) irradiation are determined by titration with 0.1 N NaOH solution. The results are calculated according to the equation

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TABLE 1

Dosimetric Characteristics of the Dicarboxylic Acids used in the Present Experiment

System	Aqueous Oxalic Acid	Solid Oxalic Acid	Solid Succinic Acid
Change observed	Decomposition of acid molecules	Decomposition of acid molecules	Destruction of initial material
Method of change measurement	Acidimetric titration or spectrophotometrically	Acidimetric titration, spectrophotometrically or by weighing of the remaining material	Weighing of the remaining material
Material to be used	50-500 mM aqueous solutions	Commercial oxalic acid dyhydrate (p. a.)	Commercial succinic acid (p. a.)
Dose range, Mrad	1.6 - 160	100 - 800	200 - 1300
Expression used for dose calculation	$D = a^{aq} c_0 \lg \dfrac{c_0}{c}$ (a)	$D = a^{ox, solid} \lg \dfrac{g_0}{g}$ (b)	$D = a^{succ} \lg \dfrac{g_0}{o}$ (b)
a	41.5 eV x molecule^{-1}	2.8×10^3 Mrad	(c)
a_n	50.0 eV x molecule^{-1}	1.0×10^3 Mrad	(c)
Upper limit of irradiation temperature, °C	80	80	100

(a) c_0 and c are the concentrations of acid before and after irradiation, respectively.

(b) g_0 and g are the weight of samples before and after irradiation, respectively.

(c) a - value is derived for the mixed pile radiation of th RA reactor
($a_{pile}^{succ} = 5 \times 10^3$ Mrad).

$$[1] \qquad D = a_{pile}^{aq} \ c_o \ lg \ \frac{c_o}{c}$$

and are presented in Table 2. The a_{pile}^{aq} is the proportionality factor for reactor radiation for aqueous oxalic acid solution, and c_o and c the concentrations of acid before and after irradiation, respectively.

(2) Solid oxalic acid

Sealed quartz ampoules containing about 0.2 g of oxalic acid dihydrate, (Merck, p.a.), were irradiated. After irradiation the ampoules were opened and kept at 95°C for 4 hours and the weights of the remaining amounts of the samples were determined. Two sets of irradiations were made. Irradiation time varied from 30 minutes to 5 hours, depending on the position. The results were calculated according to the equation

$$[2] \qquad D = a_{pile}^{ox. \ solid} \ lg \ \frac{g_o}{g}$$

and presented in Table 2. The a_{pile}^{solid} is the proportionality factor specific for oxalic acid dihydrate for reactor radiation, g_o and g the weights of samples before and after irradiation, respectively.

(3) Solid succinic acid

The procedure was almost the same as for solid oxalic acid. Sealed quartz ampoules containing about 0.2 g of succinic acid, (Merck, p.a.), were irradiated. The irradiated samples were opened and kept at 95°C for 8 hours and the weights of the amounts of the samples remaining determined. Two runs were made varying irradiation time. The expression for the absorbed dose calculation is

$$[3] \qquad D = a_{pile}^{succ.} \ lg \ \frac{g_o}{g}$$

where the notation has the corresponding meaning as in the cases above. In Table 3 only the induced chemical effect is given in the form of $lg \frac{g_o}{g}$ because the a-values for this system are not known except for the mixed pile radiation of the RA reactor (Yugoslavia)(4).

TABLE 2

Data Obtained in the GRR Reactor by Oxalic Acid Dosimeters[a]

| System | Position A-6 | | | Position B-7 | | |
	Chem. effect[b] (number of irrad.)	a_{pile}[c] $(\gamma:n)$	D_{pile} Mrad h^{-1}	Chem. effect[b] (number of irrad.)	a_{pile}[c] $(\gamma:n)$	D_{pile} Mrad h^{-1}
aqueous ox. acid	$1.614 \pm 7\%$ (2)	45.0 eV molec^{-1}	174	$0.682 \pm 10\%$ (2)	45.0 eV molec.$^{-1}$	74
solid ox. acid	$0.090 \pm 8\%$ (2)	2.1×10^3 Mrad	190	$0.049 \pm 10\%$ (7)	2.1×10^3 Mrad	84.4

(a) The values for the succinic acid dosimeter are not presented because of the lack of data. For instance, the a_{pile}^{succ} = 5×10^3 Mrad reported earlier (4) is the empirical one and valid for a particular reactor.

(b) $\lg \frac{c_o}{c}$ for liquid and $\lg \frac{g_o}{g}$ for solid systems.

(c) The values are presented in their originally published units.

TABLE 3

Chemical Effect Induced in Succinic Acid by the GRR
Reactor Radiation

Chemical Effect
(number of irradiations)

Position A-6	Position B-7
0.026 ± 5%	0.034 ± 8%
(2)	(2)

Treatment of Data

The absorbed dose measurements are evaluated according to the expression given above (equations [1]-[3]). The a_{pile}-value, which depends on the neutron and gamma contributions (at the particular position), was derived from the relation

$$[4] \qquad \frac{1}{a_{pile}} = \frac{F_\gamma}{a_\gamma} + \frac{F_n}{a_n}$$

where F_γ and F_n are the gamma and fast neutron contributions, respectively, to the total absorbed dose, and a_γ and a_n the corresponding chemical proportionality factors for each component.

The F_γ and F_n values are derived from the relations

$$[5] \qquad F_\gamma = \frac{D_\gamma}{D_{tot}} \ ; \qquad F_n = \frac{D_n}{D_{tot}} \ ;$$

$$D_\gamma + D_n = D_{tot}$$

where D_γ and D_n are the absorbed doses of gamma and fast neutron radiation, respectively, in the mixed radiation field. We used for the D_γ the calorimetric value of the absorbed dose determined in the GRR reactor during the present intercomparison measurements (6). The original D_γ in graphite was 158 Mrad h^{-1} and 76 Mrad h^{-1} for the Δ-6 and B-7 positions, respectively. It was taken and corrected for the electron density of the respective material. The D_n value was the one accepted by the editor in the present report: in aqueous oxalic acid 53 Mrad h^{-1} and 10.8 Mrad h^{-1} for Δ-6 and B-7 positions, respectively; corresponding values in solid oxalic acid are 26 Mrad h^{-1} and 5.3 Mrad h^{-1}.

The a_γ values for oxalic acid dosimeters are taken from our results reported earlier (1,2,5). As the a_n values are concerned, we have made the above calculations by introducing the values derived from ISIS (France) (7) as well as from RA (Yugoslavia) (2,3) measurements. Also, we have calculated the absorbed dose rates by using

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directly in eqs. [1] and [2] the corresponding a_{pile} values obtained experimentally in RA reactor (2,3); these are given in Table 3.

Results and Discussion

The a_{pile} values as well as the absorbed doses determined by both types of oxalic acid dosimeters are presented in Table 2. For succinic acid only the chemical effect ($lg\frac{g_o}{g}$) is given, Table 3. Small discrepancy of the measured chemical effect confirms the earlier finding on the succinic acid behaviour in in-pile irradiation, but it shows also that this sytem deserves further studies. This time, however, the absorbed doses could not be derived from the experimental data. The $a_{pile}^{succ.}$ value if calculated according to eqns. [4-6] would not correspond to the change we measured in this system, the weight loss. For it does not equal the weight of decomposed acid molecules, i.e. the change for which somewhat more is known (8).

It is interesting to compare the absorbed dose rates determined by our chemical dosimeters with those calculated from calorimetric and neutron flux measurements (Table 4). There is practically no difference between the absorbed doses obtained in these two ways in solid oxalic acid dihydrate. Aqueous oxalic dosimeter, however reveals a difference which exceeds the experimental errors. The difference in both systems increase when we introduce a_{pile} calculated by using a_n from either RA or ISIS reactor.

It is difficult to find a reasonable explanation of this based upon our present data. We do not have enough information concerning the dependence of a_n on the neutron spectrum and the choice among the available values is difficult. This is why we have preferred the above way of dose calculation. It is clear, however, that these problems deserve more in-pile intercomparative study on these and similar systems, especially concerning the neutron contribution to the dose absorbed (neutron spectrum) and the corresponding a_n value. It is hard at present to find a reasonable explanation of it, based upon the data we dispose with. It is clear, however, that these problems deserve more in-pile intercomparative study on these and similar systems.

TABLE 4

Intercomparison of Observed Dose Rates Obtained by Calculation
to Those Determined with Oxalic Acid Dosimeters

System	D Mrad h^{-1}									
	Position A-6					Position B-7				
	Calculation			chem. dos. (Table 2)	ratio[c]	Calculation			chem. dos. (Table 2)	ratio[c]
	(calorim.)	n_f	total			(calorim.)	n_f	total		
Aqueous oxalic acid	167.5[a]	53	220.5	174	1.27	82.4[a]	10.8	93.2	74	1.13
Solid oxalic acid	163.4[b]	26	189.4	190	1.0	80.4[b]	5.3	85.7	84.4	0.98

a) 250 mM oxalic acid solution equivalent doses

b) oxalic acid dihydrate equivalent doses

c) $\dfrac{\text{(absorbed dose) calculated}}{\text{(absorbed dose) measured}}$

References

1. V. Markovic and I. Draganic, Radiation Res. 35, 587 (1968).

2. V. Markovic and I. Draganic, Radiation Res. 36, 588 (1968).

3. O. Gal and I. Draganic, Int. J. Appl. Radiation Isotopes 22, 753 (1971).

4. O. Gal and P. Premovic, Int. J. Appl. Radiation Isotopes (in press) 1972.

5. O. Gal, Lj. Petkovic, Lj. Josimovic and I. Draganic, Int. J. Appl. Radiation Isotopes 19, 645 (1968).

6. A. W. Boyd, Calorimetric measurements during this inter-comparison work.

7. B. Radak, O. Gal, V. Markovic, Lj. Petkovic, M. Labrouse, J. Libmann and J. Roger, Nuclear Appl. Technology 7 (5), 409 (1969).

8. B. Radak, Lj. Petkovic and B. Bartonicek, Int. J. Appl. Radiation Isotopes 1, 77 (1969).

9. B. Radak, O. Gal, V. Markovic and Lj. Petkovic, Status report for the Meeting of the IAEA Working Group on Reactor Radiation Measurements, Grenoble, 1970.