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Dicarboxylic acids as chemical dosimeters

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AUTHOR(S)

Olga Gal

INSTITUTE

Boris Kidric Institute of Nuclear Sciences
Beograd, Yugoslavia

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INSTITUTION: "Boris Kidrič" Institute of Nuclear
        Sciences, Vinča-Belgrade, Yugoslavia

CHIEF SCIENTIFIC
INVESTIGATOR: dr Olga Gal

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PRINCIPAL INVESTIGATOR,   DIRECTOR GENERAL
             OF THE INSTITUTE,

   dr Olga Gal   dr.inž. Zdenko Dizdar

CERTIFIED BY:

DICARBOXYLIC ACIDS AS CHEMICAL DOSIMETERS

The "Boris Kidrič" Institute of Nuclear Sciences
Vinča - Belgrade, Yugoslavia

dr OLGA GAL

1. July 1971. - 1. July 1974.

S U M M A R Y

The radiolytic behaviour of dicarboxylic acids and the conditions for their dosimetric use (particularly for in--pile dosimetry) were studied. The usefulness of oxalic and succinic acid for in-pile chemical dosimetry are intercompared; results are briefly summarized in the table below

System	Succinic acid	Oxalic acid dihydrate
Dose range, Mrad	200–1300	100–800
Reactor power, MW	at least 6	up to 5
(dose rate, Mrad/hr)	(~ 70)	(~ 60)
Upper limit of irradiation temperature, °C	100	80
Reaction observed	decomposition (I order reaction)[*]	decomposition (I order reaction)[*]
Proportionality factor, [+]Mrad	$a_{succ}=5.0 \times 10^{-3}$	$a_{ox}=2.11 \times 10^{-3}$
Method of analysis	weighing of the remaining substance	weighing of the remaining substance
Initial sample amount, gramme	≤ 0.5	≤ 0.2
Accuracy	better than 10 per cent	
Relative ease for routine use	about the same	

[*]$D(Mrad) = a \log g_0/g$, where g_0 and g are the weights of acids before and after irradiation, respectively.

[+]For the RA reactor at Vinča (Yugoslavia); mixed pile radiation, gamma to neutron ratio 70/30 in water.

Since the radiolysis of succinic acid was shown to be more complicated, part of the work was concentrated to the details of the radiolytic mechanism. It was shown (unexpactedly) that CO_2^- radical does not exist in this compound when irradiated at the ambient temperature.

The other part of the work was devoted to the influence of different kinds of incident radiation on the radiolysis of the above mentioned compounds. Their dosimetric behaviour was intercompared with cyclohexane in the GRR-1 reactor with the reference to the calorimetric values (denoted as "predicted" in the table) obtained in the same experiment. From the table below one can see that the first three systems reasonably agree whereas the third one (succinic acid) needs more study in order to obtain more accurate dose-effect proportionality factors.

Irradiation position	Mrad h^{-1}			
	Cyclo-hexane	Oxalic Aqueous	Oxalic Solid	Succinic Acid
Δ- 6 (obtained)	110	80.0	56.7	75.4
Obtained/Predicted	1.20	1.03	0.99	1.30
β- 7 (obtained)	35.9	29.8	23.2	31.2
Obtained/Predicted	1.05	0.96	0.96	1.28

In order to study the LET effects on the radiolysis in solid oxalic acid the powdered mixtures of Li-oxalate and oxalic acid were irradiated in the reflector of reactor core. The incident radiation were the heavy charged particles from ^{6}Li(n, alpha)^{3}H reaction, and the net decomposition of oxalic acid as well as the CO_2 formation as a function of absorbed dose were measured. The measured G values pointed out that the radiolysis under these conditions proceeds at a decreased rate. The reliability of these results are discussed on the basis of neutron fluence measurements (absorbed dose) and on the effectiveness of the use of energy released in the nuclear reaction.

Radiolysis of the solid Li-acetate was shown to be suitable for studying phenomena such as the formation of free radicals. In the gamma irradiated single crystals of this compound two radicals are identified, i.e. $CH_2CO_2^-$ and $RCHCO_2^-$, by the methods of ESR, UV and IR spectroscopy.

SCIENTIFIC PART OF THE REPORT

In the present project the radiolytic behaviour of di-carboxylic acids as well as the conditions for their use in chemical dosimetry were studied. Since they did not get activated by the thermal neutrons these compounds are particularly suitable for reactor irradiations. Another favourable feature for in-pile use is their low decomposition by radiation. The first homologue, oxalic acid, has been thoroughly studied and was proposed as a chemical dosimeter in the solid state as well as in aqueous solution. It has already been used successfully under certain conditions.

Two approaches have been chosen in the present investigation. In the first the systems were emphasized, i.e.:

- for oxalic acid, to look for more accurate knowledge on some essential dosimetric parameters as e.g. the temperature dependence, dose rate, reproducibility;

- for other similar systems, to estimate and check their possible advantages as compared to oxalic acid.

The second approach was of particular interest for reactor dosimetry - the kind of radiation was emphasized and its influence on the irradiation system studied.

I CHEMICAL SYSTEMS

I.1. - A comparative study of solid oxalic and succinic acid has been carried out. The latter one was chosen because it stands higher temperatures and radiation levels, which enabled its dosimetric use at higher reactor powers. Yet thanks to the simple and reliable method for the measurement of chemical change (decomposition), oxalic acid is still a more suitable system for the routine, in-pile dosimetry. The results of these investigations are published in the paper

O. GAL and P. PREMOVIĆ, "SOLID DICARBOXYLIC ACIDS AS IN-PILE CHEMICAL DOSIMETERS", Intern.J.Appl.Rad. Isotopes, 23, 341 (1972).

I.2. - The radiolytic mechanism of succinic acid is somewhat more complicated. In spite of the number of studies devoted to this problem, there are still some phenomena and stages in its decomposition process which are not well understood. Since a better knowledge of the radiolytic processes in a potentially promising dosimetric system is of importance for its practical use, we directed our attention to some

phenomena caused by the radiation action on this system. In such a way we came to the conclusion that at the room temperature does not exist the CO_2^- radical - a[^species which was believed to] have an influence on the radiolytic mechanism. These results are published in the paper

P. PREMOVIĆ, O. GAL and B. RADAK, "ON THE ABSENCE OF CO_2^- IN IRRADIATED SUCCINIC ACID", J.Chem.Phys., 59, 987 (1973).

II RADIATION FIELD

II.1. - Since the dicarboxylic acids are suitable for the use in reactor core it was of interest to look on their behaviour in different reactor i.e. the sources of different radiation fields (the type of spectra). In this connection we took part (O. Gal and I. Draganić - Report DEMO 74/5, 1974) in the international intercomparison measurement organized by the IAEA in July 1972, in Athens (Greece). Another set of measurements we (O. Gal and B. Radak) performed at GRR-1 reactor (Athens) in November 1973. The aim of the latter experiment was to calibrate some similar chemical systems in a particular radiation field which different from the one in which the same systems were previously tested. The results pointed out that each particular system has first to be checked in the given reactor core in order to be used in it routinely. The need for further studies of the influence of radiation spectra (gamma rays and neutrons) was also emphasized. The results were summarized in the papers:

B. RADAK, O. GAL, D. MARKETOS and A.W. BOYD: "INTERCOMPARISON OF DICARBOXYLIC ACIDS, CYCLOHEXANE DOSIMETERS AND CALORIMETERS IN THE GREEK RESEARCH REACTOR - NOVEMBER 1973., GREEK ATOMIC ENERGY COMMISSION, NRC "DEMOCRITOS", Report DEMO, 74/8 (1974).

B. RADAK, O. GAL, D. MARKETOS and A.W. BOYD: "INTERCOMPARISON IN-PILE DOSIMETRY IN GRR-1. CALORIMETERS AN CHEMICAL DOSIMETERS: CYCLOHEXANE AND DICARBOXYLIC ACIDS" (Letter to the Editor), Submitted for publication in Int.Journ.Appl.Rad. and Isotopes.

II.2. - With regard to the use of dicarboxylic acids in nuclear reactors a part of the work has been devoted to the study of decomposition of solid oxalic acid by the heavy charged particles from reaction $^6Li(n, alpha)^3H$. The problem is bound to a more general one i.e. the dependence of the radiolysis of solid oxalic acid on the LET value of incident ra-

diation. The powdered mixtures of Li-oxalate and oxalic acid
of different mol fractions were irradiated in the reflector
of the RA reactor and the decomposition of oxalic acid and
formation of CO_2 was followed as a function of absorbed dose.
The radiation chemical yields of both decomposition and CO_2
formation point out that the radiolysis by the heavy charged
particles (alpha and ^3H) proceeds at a considerably decrea-
sed rate. Considering the effectiveness of the use of energy
released in the given nuclear reaction, a model is given by
which it was shown that the energy loss under the given con-
dition can not exceed 20 per cent. The details of this rather
elaborate investigation are given in the paper

O. GAL and B. RADAK: "DECOMPOSITION OF SOLID OXALIC ACID
BY HEAVY CHARGED PARTICLES from $^6Li(n, alpha)^3H$ REACTION (pre-
pared for publication).

II.3. - With an intention to measure the absorbed dose
from $^6Li(n, alpha)^3H$ in the thermal neutron field an attempt
was made to follow the radiolysis of solid Li-acetate. It was
shown that this system is more suitable to study the phenome-
na, hence these studies were emphasized in this part of the
work. The possibilities of comparative spectroscopic measure-
ments were particularly analysed because of their importance
in the study of radiation-chemical processes. These results
are published in the paper

P. PREMOVIĆ and O. GAL: "ESR AND OPTICAL SPECTRAL STUDI-
ES OF GAMMA-IRRADIATED LITHIUM ACETATE DIHYDRATE", Chemical
Physics Letters, <u>25</u>, 571 (1974).

FINANCIAL PART OF THE REPORT

The contract covered three years period: 1. July 1971.-
-1. July 1974.

Total amoun of the project budget in US $:

per year	for 3 years
16.000.-	48.000.-

The amount of the grant (25% of the total amount) contributed
by the Agency, equivalent to US $

	per year	total/3 years
Salaries & Wages	2.000.-	6.000.-
Expanable Supplies	800.-	2.400.-
Services and other costs	1.200.-	3.600.-
Total	4.000.-	12.000.-

PRINCIPAL INVESTIGATOR,

O. Gal

dr Olga Gal

RESPONSIBLE FINANCIAL
OFFICIAL,

dipl.ec. B. Dedović

$\underline{\text{II}} . 1_a$

DEMO Report 74/8 (1974)

INTERCOMPARISON OF DICARBOXYLIC ACIDS CYCLOHEXANE DOSI-
METERS AND CALORIMETERS IN THE GREEK RESEARCH REACTOR
NOVEMBER 1973

by

B.B.RADAK and O.S.GAL, Boris Kidrič Institute of Nuclear
                    Sciences, Vinča, Yugoslavia

D.G.MARKETOS, Nuclear Research Center "Democritos" Athens,
                    Greece

A.W.BOYD, Chalk River Nuclear Laboratories, Chalk River, Canada

INTRODUCTION

Measurement of the absorbed dose in the mixed radi-
ation field of a reactor core by the use of chemical changes
in suitable systems is not a recent approach to the problem.
A number of well established chemical dosimeters exist which
have been recommended for in-pile use[1]. However, their beha-
viour in different reactor cores has not been tested systemati-
cally, or more precisely, the number of comprehensive experiments
of this kind is still rather limited. Practically, there is a ne-
ed of intercomparison of calibration values of the same chemical
systems in different reactor cores, i.e., in fields having dif -
ferent neutron and gamma spectra and different corresponding con-
tributions to the total absorbed dose[2]. By calibration we mean
obtaining dose-chemical effect plots for chemical systems at a
position in the core where not only the total absorbed dose but
also the contributions of neutrons and gamma rays are accurately
known.

An intercomparison of such data obtained at different
reactors could lead to the choice of chemical dosimeters for the
more general use. Such an attempt was made in 1968, at ISIS re-
actor (Saclay, France)[3,4] where the absorbed dose calibration
was made by calorimetry, fast neutron fluence by treshold detec-
tors (In, Ni, Al), and the chemical systems (dicarboxylic acids)
calibrated at the RA reactor (Vinča, Yugoslavia) tested. A simi-
lar experiment on a wider scale was performed in 1972, at the
GRR-1 reactor (Athens, Greece)[5] where the totally absorbed do-
se was estimated from calorimetric values in graphite and fast
neutron fluence (Ni-detectors), on the basis of which eight dif-
ferent chemical dosimeters from different IAEA member states we-
re checked. The present experiment was undertaken to clarify the
discrepancies in the results of this intercomparison. For deter-
mination of the total dose and its neutron and gamma component

in light materials, calorimetric measurements in graphite and
polyethylene were chosen; to check the magnitude of the neutron
component the fast neutron fluence was measured (Ni-detectors);
chemical systems: cyclohexane, oxalic acid solid and in aqueous
solution and succinic acid were then irradiated in the calibrated
position. The choice of chemical systems was made having in mind
their features relevant to the intercomparison work. Cyclohexane
is a dosimeter in which the radiolytic yield, $G(H_2)$, does not
depend on the LET of the radiation; also its formula is, dosime-
trically, the same as that of polyetylene, hence the possibility
of direct intercomparison of calorimetric and chemical results.
Oxalic acid in aqueous solutions is a dosimeter which has been
thoroughly investigated in different radiation fields, particu-
larly in reactor cores; solid oxalic acid has been shown to be a
promising in-pile dosimeter in the range of very high doses.
Succinic acid was interesting because of its stability at eleva-
ted temperatures.

EXPERIMENTAL

Measurements were made in the GRR-1 reactor[5] (highly
enriched, light water moderated and cooled, nominal power 5 MW).
The irradiations were done in the positions A-6 and B-7 (Fig.1).
Dry channels i.e. watertight aluminum tubes (i.d. 30 mm o.d.
32 mm) were installed in these positions. Plugs were inserted
in these tubes to align the vertical centres of the calorimeter
with the vertical centres of the fuel elements.

The Vinča - calorimeter[3,4,6], a differential device
divided into stages, having polyethylene and graphite as thermal-
ly active bodies, was used. Each calorimeter, hanging on its ca-
ble was manually lowered to the irradiation position in the tube.

Chemical samples were in aluminum wire baskets suspen-
ded by a nylon thread, and were inserted manually. The baskets

were adjusted so that the centerline of the samples corresponded
to that of the fuel. The treshold detectors were irradiated in
a similar fashion.

To avoid overheating of the samples the reactor was
limited to 1 MW. At this power the temperature of the polyethyle-
ne in the calorimeter does not exceed $80^{\circ}C$.

The preparation of the chemical samples was done as
described in earlier references [1,7,8,9,10].

RESULTS

Three calorimeters were used: one contained a piece
of graphite and a calibration heater in an aluminum capsule which
formed the calorimetric body, the second contained polyethylene
and a heater in the capsule of the same weight and shape and the
third one ("empty") contained only an aluminum capsule and a he-
ater. In each of the calorimeters the total radiation energy de-
position rate, P_{tot} (mW), was measured and then the rate of the
"empty" one was subtracted from the values obtained with polyet-
hylene and graphite. In this way the net absorbed dose rates,
F (mW/G), in graphite and polyethylene were obtained. These va-
lues are listed in Table 1. ΔT (μV) represents the equilibrium tem-
perature difference between the body and jacket; it is expressed
as the measured response in microvolts of a copper-constantan
thermocouple.

The chemical samples were irradiated at the same po-
sitions. The liquid samples (oxalic acid solutions and cyclohe-
xane) were irradiated separately, whereas the solids were grou-
ped: two ampoules of oxalic and one of succinic acid in each ir-
radiation. After irradiation they were treated and analysed as
described previously in references [1,7,8,9,10]. For cyclohexane
a linear relationship between the hydrogen produced and absorbed
dose was assumed, $G(H_2)$ depending slightly on the total absorbed
dose. The data are presented in Table 2 and Fig.2.

In the case of dicarboxylic acids there is a logarithmic relationship both in solutions and in the solid state[7,8,11]. For aqueous solutions

$$D = a_{aq} \ Co \ \log C_o/C \tag{1}$$

where a_{aq} is the proportionality factor for aqueous solution of oxalic acid which depends on the neutron - to - gamma ratio in the absorbed dose, C_o the concentration before and C after irradiation. For solids

$$D = a_{solid} \ \log g_o/g \tag{2}$$

where a_{solid} has the same meaning as above and is different for different solids, g_o and g are the masses of the sample before and after irradiation. The data obtained with dicarboxylic acids are presented in Tables 3 and 4 and Figures 3 and 4.

The fast neutron fluence was determined from the activity of Ni foil detectors irradiated at different heights around the center line of the fuel. Data on these measurements are presented in Table 5. By plotting the flux intensities as a function of height the corresponding values for the center line position are derived as

in 4 - 6 $1.95 \times 10^{12} \ n \ cm^{-2}s^{-1}$

in 5 - 7 $0.43 \times 10^{12} \ n \ cm^{-2}s^{-1}$

Thermal neutron flux densities were determined from the activities of Au foils with and without Cd shielding (Cd ratio = 6). It was estimated as

in   - 6 $\phi_{th} = 0.97 \times 10^{13} \ n \ cm^{-2}s^{-1}$

in   - 7 $\phi_{th} = 2.93 \times 10^{12} \ n \ cm^{-2}s^{-1}$

Based on the data from ref (15) one calculates that in any of our hydrogenous samples the absorbed dose from reaction N(n,gamma)N

could contribute to less than 1 per cent of the totally absorbed
dose. This source of gamma radiation was therefore neglected in
further considerations.

TREATMENT AND DISCUSSION OF RESULTS

A.- Calorimetry

If P_c and $P(CH_2)_n$ are the total absorbed doses in
graphite and polyethylene then

$$P_c = G + F \tag{3}$$

$$P_{(CH_2)_n} = aG + bF \tag{4}$$

where G and F are the gamma and fast neutron contributions to
the absorbed dose in graphite (used here as a reference materi-
al), and a and b are the ratios of mass energy transfer coef-
ficients of these two materials for gamma rays and fast neutrons
respectively. The accuracy of G and F obviously depends on the
difference between P_c and $P_{(CH_2)_n}$, but also on exact knowledge
of a and b. Since for gamma rays the relative mass energy tran-
sfer coefficients for light materials are fairly constant over
wide range of energies, the a coefficients are well established.
The b coefficient one evaluates on the basis of non-thermalized
neutron spectrum and the cross section for elastic scattering
of neutrons in the respective material. Since the form of the
neutron spectrum in an experimental hole is rarely exactly known,
it generally has to be assumed in order to calculate the b value.
This might lead to considerable errors in G and F values. In or-
der to find the limits of possible discrepancies we calculated
the a values in three ways:

I.- combining the assumed fission spectrum with
the data on the mass energy coefficients for
different elements from reference (1);

II.- combining the assumed dE/E spectrum with the
same data;

III.- by evaluation from the detailed diagrams from
ref. (12).

In all cases the material treated was polyethylene relative
to graphite. The b values obtained are

	$A - 6$	$\beta - 7$
Method I	10.9	10.9
Method II	11.5	11.5
Method III	9.1	9.0

The a value for polyethylene amounts to 1.14 and is obtained
from mass absorption coefficients for hydrogen and carbon in
the gamma energy range from 100 keV to 3 MeV. Taking these va-
lues and the measured P_c and $P_{(CH_2)_m}$ from Table 1

	$A - 6$		$\beta - 7$	
P_c	138.2 mW/g = 49.8 Mrad/h		60.7 mW/g = 21.0 Mrad/h	
$P_{(CH_2)_m}$	250 mW/g = 90.0 Mrad/h		96.2 mW/g = 34.5 Mrad/h	

the values listed in Table 6 are obtained. Although extreemly
different spectral distributions were assumed one may see that
the differences in results are rather small. It is possibly due
to the fact that by evaluating the relative values over the
broad energy region the differences appearing at some values of
energy increment do not make a significant contribution to the
total value.

The reliability of calorimetric measurements was chec-
ked by evaluating the neutron contribution from the measured
fast spectrum and comparing it to the corresponding values deri-
ved from calorimetry. This was done in several ways.

ASTM Recommendations, as described in ref (13) and
briefly by K.C. Humphreys in ref (5). Based upon the type of
spectrum (fission or dE/E) and the neutron interaction cross
section for the elements of interest one derives the absorbed

dose per neutron (Dpn) in a given material. This value is then multiplied by the total non-thermalized neutron spectrum in order to obtain the absorbed dose from neutrons

$$F_M = \frac{Dpn \cdot \phi f}{f_f} \tag{5}$$

where F_M denotes the neutron contribution to the absorbed dose in a material M, ϕf neutron flux density in the region E>1 MeV, f_f fraction of neutrons having E>1 MeV in the total assumed spectrum.

C.E.A. Method, derived by F. Has and Y. Droulers[12] consists of simple multiplication of a coefficient $\Gamma(x,M)$ with the experimental value of ϕf

$$F_M = \Gamma(x,M) \phi f \tag{6}$$

where x denotes the distance from the core and M refers to material of a given atomic composition. In reference (12) there are detailed diagrams for Γ-values for hydrogen, carbon and oxygen wherefrom one easily derives the Γ values for most of the materials of interest.

Combined Method, by assuming that above E=1 MeV there is a fission spectrum, whereas below it there is a $dE/[N \sigma(E)]$ form[12]. Here $\sigma(E)$ denotes the neutron cross section for elastic scattering on hydrogen. One distributes the ϕf neutrons in energy intervals above 1 MeV and multiplies these with the corresponding mass energy transfer coefficients from the tables of reference (1). For the energy interval below 1 MeV one takes that at 1 MeV (or any other value around it) both spectral forms have the same value, i. e.

$$\lambda \left[\frac{dE}{E \sigma(E)} \right]_{E=1 \text{ MeV}} = \left[\phi f \, dE \right]_{E=1 \text{ MeV}} \tag{7}$$

and derives the constant λ, i.e. the intensity coefficient of the spectrum below 1 MeV. The general expression for the absorbed

dose from neutrons in a material is

$$F = \frac{2 N_o}{(A+1)^2} \int \phi(E) \ \sigma(E) \ E \ dE \tag{8}$$

where N_o is Avogadro's number, A the atomic number of the element the material is composed of, other symbols are as defined above. It is obvious that with the assumed spectral form

$$F_{E<1 \ MeV} = \frac{2 N_o \lambda}{(A+1)^2} \tag{9}$$

dE/E Assumption. If a spectrum of this form is assumed over the whole energy region, one can see from the expression (8) that

$$F = \frac{2 N_o \lambda}{(A+1)^2} \int \sigma(E) \ dE \tag{10}$$

λ is found from

$$\int_{1 \ MeV}^{E(MeV)} \lambda \frac{dE}{E} = \phi f \tag{11}$$

and the value of integral for the cross section one obtains by numerical integration of the cross section data[14]. This approach depends on the upper limits of integration.

Values of neutron contributions in polyethylene derived in different ways are intercompared in Table 7, where the values from Table 6 are also tabulated. One can see that for the A-6 position a better approach is the one which assumes the fission spectrum, whereas for β-7 a better agreement is obtained with a dE/E spectrum. This is in accordance with the fact that A-6 is quite close to the core, i.e. in a less perturbed neutron flux, whereas β-7 is separated from the core by more than 10 cm of water.

B.- Chemical Systems

Among the chemical dosimeters used the simplest was cyclohexane. The radiolytic yield of hydrogen, $G(H_2)$, was found to be independent of LET value of incident radiation[15]. It was important because of the high abundance of hydrogen in this compound and hence a high neutron (i.e. knocked-on proton) compo - nent in the absorbed energy. A slight decrease in the yield was reported[10] which was taken into account in evaluation of absorbed doses. From the data in Table 2 and taking the density of cyclohexane as 0.78 one obtains the results in Table 8. It follows that the dose rates are

for $\Delta - 6$ 110   Mrad h^{-1}

for $\beta - 7$ 35.9   Mrad h^{-1}

with an average deviation of 2.5%. Taking $G(H_2) = 5.0$ independent of dose, the average values are

for $\Delta - 6$ 107   Mrad h^{-1}

for $\beta - 7$ 36.1   Mrad h^{-1}

and the deviation increased to 4%. One can directly compare these values with the calorimetric readings in polyethylene, because both compounds have the same empirical formula. A comparison with the Table 6 shows a reasonable agreement in $\beta-7$ (better than 5%), but in $\Delta-6$ the cyclohexane values are about 20% higher than calorimetry "predicted". It does not seem, with our present knowledge, that a reasonable explanation for this deviation can be given. Regarding the interactions with various types of radiation, and hence the absorbed energy, cyclohexane and polyethylene are the same. The agreement in $\beta-7$ reflects this fact, although the calorimetric value in polyethylene is slightly lower. Let us suppose that it is due to some endothermic reactions in polyet - hylene (e.g. hydrogen evolution due to the cross linking) and say

that one might expect this is more pronounced in a radiation
field with higher LET. Even in such an imagined case it seems
that 20 per cent difference can hardly be expected.

Since the dicarboxylic acids are LET dependent,
one had to calculate the a - values from a_{gamma} and $a_{neutron}$
[1,16] and the known neutron, F_n, and gamma, F_{gamma}, contribu-
tions to the absorbed energy

$$\frac{1}{a} = \frac{F_n}{a_n} + \frac{F_{gamma}}{a_{gamma}} \tag{12}$$

We used the following values for oxalic acid

	In water	Solid
a_{gamma}	41.5 eV molecule^{-1}	2.8×10^3 Mrad
a_n	58.0 eV molecule^{-1}	1.0×10^3 Mrad

For succinic acid the value obtained at the BR reactor[17], i.e.
$a^{succ.} = 5 \times 10^3$ Mrad, was used. Three sets of results were com-
pared:

A.- calculated on the basis of an assumed distribution
among neutrons and gammas;

B.- taking the distribution, i.e. F_n and F_{gamma}
as derived from calorimetry;

C.- evaluated on the basis of calorimetric data
in graphite and polyethylene, by using a and
b coefficients for the respective compound.

These results are summarized in Table 9. The fractions F_n (and
$F_{gamma} = 1-F_n$) used in the calculations are

	Oxalic aqueous		Oxalic solid	
	A - 6	B - 7	A - 6	B - 7
A	0.50	0.20	0.20	0.10
B	0.35	0.26	0.18	0.13

In order to intercompare the usefulness of the four chemical systems applied in the present work, their results are compared with the values derived, for the respective compounds, from calorimetric data obtained with graphite and polyethylene. Values are presented in Table 10, in which for oxalic acid the calorimetrically obtained distribution of the neutron and gamma components were used. Except for succinic acid and cyclohexane in Δ-6, the agreement of the results is acceptable. The cyclo-hexane case was discussed above and as for as succinic acid is concerned it seems that more work is still needed to determine a more reliable a value. The value of 5×10^3 Mrad used here is taken from the RA measurements, i.e. it was obtained in a diffe-rent reactor core. This however could not influence considerably the results obtained, since the neutron component in both RA and GRR-1 is rather low in succinic acid. On the other hand, the loss of weight of succinic acid, although the simplest way in routine use, is not the real measure of its decomposition as it is in the case of oxalic acid. It seems therefore that some experiments related to the treatment of samples and analytical method (maybe higher temperature of heating prior to analysis and acidimetric titration) might contribute to the clarification of the problem.

CONCLUSIONS

A chemical system is not an absolute dosimeter, i.e. it needs calibration for each type of radiation field in which it is to be used. Once calibrated it can be used, even routinely, as a secondary standard. The use of chemical dosimeters is gene-rally simpler than that of any other type of dosimetric devices, and therefore a desire for their wider use is quite logical.

An attempt to make a chemical system suitable for in-pile measurements, i.e. for a two-component radiation field is somewhat different than for the simpler one-component cases. The shortest way to do this in a field composed of neutrons and gamma radiation is:

- to calibrate it against another dosimeter (chemical, cavity chamber, or calorimeter) in a gamma field; the value obtained is then considered as independent of the gamma spectrum;

- to calibrate it against a calorimeter in the actual mixed field; this calorimeter must contain the same compound as the absorbing body, or better, to use the calorimeters for measurements of the absorbed energy contributions of neutron and gamma radiation.

At this stage the chemical system is calibrated for a particular field. One can use it in fields, having different neutron-to-gamma ratios only after additional calibrations. The present experiment was one of such attempts.

Rigorous calorimetric measurements were essential. Therefore two light materials with different responses to neutrons (for gamma rays all materials show a similar energy absorption) were chosen: graphite and polyethylene. Moreover, as a check the fast neutron energy contribution was determined from measurements of the fast neutron flux density. In this way the reliability of calorimetric values was proven. Therefore these values and the ones derived from them(absorbed doses in other light materials) were taken as "standards" for comparison. One has to note here also that both the interpretation of calorimetric data and the checks on these data contain some arbitrary elements such as the type of neutron spectrum and the energy region assumed for evaluations of coefficients. It is difficult to obtain the exact form of the whole non-thermalized neutron spectrum, particularly in the region below 1 MeV which is of considerable importance for hydrogeneous materials. A result of the present work was the study of deviation limits by using several possible assumptions.

Chemical systems developed for in-pile measurements were used here. Cyclohexane has been thoroughly investigated in different radiation fields and its independence of LET has been well established. In addition, it has been applied as an in-pile dosimeter in several reactors.

The 20% discrepancy in its value in ~6 is therefore surprising and shows that some direct intercompartison measurements (e.g. calorimetry with these two materials) are still needed. Oxalic acid showed good agreement this time both as solid and in solution. Even the values obtained on the basis of a guessed neutron-to-gamma ratio, i.e. by an evaluation which could be expected in routine work, are acceptable. With these systems one could be completely satisfied if the results obtained at the ISIS reactor did not exist$\left(\frac{16}{7}\right)$. In that case the aqueous solution gave some 40% lower results than calorimetry predicted; the solid gave about 10% lower. It is obvious that more combined experiments as the present one, are needed. Maybe the measurements in experimental holes at different distances from the core, i.e. containing different neutron contributions, are the most promising. In that way a stepwise connection between the pure gamma and in-core radiation field could be obtained. Succinic acid showed both now and in the ISIS experiment about 40% higher values than those derived from calorimetry. As stated above, this attractive dosimeter (low sensitivity to the temperature, high dose range) needs more study to obtain an accurate a value. Some of our earlier experiments[18] show that the a value could be considerably lower than 5×10^3 Mrad which, if true, could decrease the discrepancies with calorimetry to reasonable values.

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REFERENCES

1.- A.W.Boyd (editor), Determination of Absorbed Dose in Reactors
    IAEA Technical Reports Series No.127 (1971).

2.- Meeting of the IAEA Working Group on Reactor Radiation Measu-
    rements Grenoble, France (1970).

3.- B.Radak, O.Gal, V.Marković, Lj.Petković,M.Labrousse, J.Libmann
    and J.Roger, Nucl.Appl. Technology, $\underline{7}$, 409 (1969).

4.- M.Labrousse, J.Libmann, J.Roger, B.Radak, O.Gal, V.Marković
    and Lj.Petković, C E A - N - 1168 (1969).

5.- D.G.Marketos and A.W.Boyd (editors), International Intercom-
    parison of Chemical Dosimeters for In-Pile Use, Greek Atomic
    Energy Commission Nuclear Research Center Democritos Report
    DEMO 74/5 (1974).

6.- A.W.Boyd (editor), International Intercomparison of Calori-
    meters, IAEA Technical Reports Series No.128 (1970).

7.- V.Marković and I.Draganić, Rad.Res. $\underline{36}$, 588 (1968).

8.- O.Gal, Ph.D.Thesis, University of Beograd (1967).

9.- O.S.Gal and I.G.Draganić, Int.J.Appl.Rad and Isotopes,$\underline{22}$,
    753 (1971).

10.- A.W.Boyd, H.W.Conor and J.J.Pieroni, CRNL Report AECL-2203
    (1965).

11.- I.G.Draganić and O.S.Gal, Rad.Res.Rev., $\underline{3}$, 167 (1971).

12.- P.Mas and Y.Droulers, Raport C E A - R 2510 (1964).

13.- ASTM Standards, Annual Book, Part 27 (1970).

14.- United States Atomic Energy Commission Report B N L 325.

15.- W.G.Burns and J.R.Parry, Nature, $\underline{201}$, 814 (1964).

16.- V.Marković, Ph.D.Thesis, University of Beograd (1968).

17.- O.Gal and P.Premović,Int.J.Appl.Rad.and Isotopes,$\underline{23}$,541(1972).

18.- B.Radak, Lj.Petković and B.Bartoniček, Int.J.Radiat.Phys.Chem.
    $\underline{1}$, 77 (1969).

19.- J.K.Linacre,C.R.V.Reed,N.K.Taylor and R.B.Thomas,AERE-R 4807
    (1965).

Table 1. Data on Calorimetric Measurements
(GRR-1 Reactor Power 1 MW)

Calorimeter	Irradiation Position					
	A - 6			B - 7		
	ΔT (μV)	P_{tot} (mW)	P (mW/g)	ΔT (μV)	P_{tot} (mW)	P (mW/g)
Empty Sensitivity: 5.40 μV/mW	810	150	–	345	64	–
Graphite Sensitivity: 5.35 μV/mW Body:0.5934 g	1235	232 82	– 138.2	535	100 36	– 60.7
Polyethylene Sensitivity: 5.35 μV/mW Body:0.4678 g	1420	267 117	– 250.0	580	109 45	– 96.2

Table 2. Data on Cyclohexane Measurements

(GRR-1 Reactor Power 1 MW; Samples of 1 ml Cyclohexane)

Length of Irradiation	H_2 Molecules Formed	G -Value for Calculation of Dose
P o s i t i o n A - 6		
2	9.19×10^{18}	5.13
3	1.35×10^{19}	4.94
4	1.65×10^{19}	4.85
5	2.10×10^{19}	4.74
6	2.56×10^{19}	4.66
P o s i t i o n B - 7		
4	6.25×10^{18}	5.33
6	9.01×10^{18}	5.13
8	1.41×10^{19}	5.0
10	1.48×10^{19}	4.87
12	1.61×10^{19}	4.83

Table 3. Results of the Measurements with Aqueous
Solution of Oxalic acid

(GRR-1 reactor power 1 MW; $C_o = 250$ mM)

Length of Irradiation (min)	log C_o/C	Length of Irradiation (min)	log C_o/C
Position A - 6		Position B - 7	
6	0.0948	15	0.092
15	0.175	30	0.133
23	0.268	42	0.175
30	0.353	45	0.208
36,5	0.449	60	0.258
45	0.606		

Table 4. Results of the Measurements with
Solid Dicarboxylic Acids

(GRR - 1 reactor power 1 MW)

Length of Irradiation (n)	$\log g_o/g$			
	Oxalic Acid Dihydrate		Succinic Acid	
	$\Delta - 6$	$\beta - 7$	$\Delta - 6$	$\beta - 7$
2.25	0.0675	-	-	-
2.25	0.0657	0.0225	0.0427	0.0200
2.95	0.0980	0.0314	-	-
2.95	0.0980	0.0310	0.0470	0.0200
6.00	0.1740	-	-	-
6.00	0.1640	-	-	-
7.67	-	0.0704	-	-
7.67	-	0.0712	0.0890	0.0438

Table 5. Results of Ni Foill Irradiations
(GRR-1 reactor power 1 MW; Exposure 12.00 min.;
from 13:48 to 14:00 East European Time,
November 8. 1973)

Foil Weight (mg)	Distance from Centre Line of Fuel (mm)	DPS/mg Nov.8/73.	Fast Neutron Flux Intensity >1 MeV ($n\ cm^{-2}\ s^{-1}$)
Position A- 6			
51.95	− 24	176.46	2.013×10^{12} *
52.42	− 5	169.73	1.936×10^{12}
48.60	+ 15	169.44	1.933×10^{12}
53.50	+ 34	161.20	1.839×10^{12}
Position B − 7			
53.66	− 25	42.46	0.453×10^{12} *
49.30	− 7	39.80	0.427×10^{12}
53.36	+ 12	39.94	0.428×10^{12}

* Taking a cross section for $^{58}Ni(n,p)^{58}Co$ of 155 mb for
A − 6 and 165 mb for B − 7

Table 6. Gamma and Fast Neutron Contributions to the Absorbed
Dose Obtained by Different Treatments of Calorimetric
Results

$$(\text{Mrad h}^{-1})$$

Material	Position A-6			Position B-7		
	Neutron	Gamma	Total	Neutron	Gamma	Total
Method I						
Graphite	3.4	46.4	49.8	1.0	20.8	21.8
Polyethylene	37.2	52.8	90.0	10.8	23.7	34.5
Method II						
Graphite	3.2	46.6	49.8	0.94	20.9	21.8
Polyethylene	36.9	53.1	90.0	10.8	23.7	34.5
Method III						
Graphite	4.15	45.6	49.8	1.24	20.6	21.8
Polyethylene	37.8	52.2	90.0	11.2	23.3	34.5

Table 7. Neutron Contribution to the Absorbed Dose in Polyethylene Derived in Different Ways   (Mrad h^{-1})

Derived by	Irradiation Place	
	A - 6	B - 7
Calorimetric Measurements. Method I and II	37.0	10.8
Calorimetric Measurements. Method III	37.8	11.2
ASTM Procedure Fission Spectrum	39.6	8.64
ASTM Procedure dN/E Spectrum	45.6	9.70
C.E.A. Method	44.0	9.55
Combined Method >1 MeV Fission <1 MeV $\frac{dE}{N_{\phi}(E)}$	44.0	9.66
Combined Method dN/E spectrum	49.3	11.9

Table 8. Dose Rates Derived from Cyclohexane by using the Data from Table 2. $|\text{Mrad } h^{-1}|$ (Cyclohexane density 0.78)

Length of Irradiation (min)	A - 6	Length of Irradiation (min)	B - 7
2	110.5	4	36.2
3	112.4	6	36.1
4	105.0	8	35.2
5	108.9	10	37.5
6	113.0	12	34.3

Table 9. Results of Dosimetry with Dicarboxylic Acids

$|\text{Mrad } h^{-1}|$

Way of Evaluation	Oxalic Aqueous		Oxalic Solid		Succinic Solid	
	A-6	B-7	A-6	B-7	A-6	B-7
A	84.4	29.1	58.5	24.3	75.4	31.2
B	80.0	29.8	56.7	23.2	-	-
C	77.4	31.0	57.4	24.3	57.4	24.3

Table 10. Comparison of the Values Obtained by Chemical
Dosimeters to the ones "Predicted" by
Calorimetry

$$[\text{Mrad h}^{-1}]$$

Dosimeter	Obtained		Predicted	
	$\Delta \sim 6$	$\beta - 7$	$\Delta - 6$	$\beta - 7$
Cyclohexane	107	36.1	90.0	34.5
Oxalic Aqueous	80.0	29.8	77.4	31.0
Oxalic Solid	56.7	23.2	57.4	24.3
Succinic Acid	75.4	31.2	57.4	24.3

	Obtained / Predicted	
	$\Delta - 6$	$\delta - 7$
Cyclohexane	1.19	1.05
Oxalic Aqueous	1.03	0.96
Oxalic Solid	0.99	0.96
Succinic Acid	1.30	1.28

LEGEND TO THE FIGURES

Fig.1.- The Greek Reasearch Reactor Core Arrangement.

[X] Fuel elements

[ ] Vacant lattice positions

Fig.2.- Experimental data obtained with cyclohexane;
--o-- Δ-6, --x-- β-7

Fig.3.- Experimental data obtained with aqueous solution of
oxalic acid (250 mM); --Δ-- Δ-6, --o-- β-7

Fig.4.- Experimental data obtained with solid dicarboxylic acids;

- Δ - Oxalic in Δ- 6
- o - Oxalic in β- 7
- $\blacktriangle$ - Succinic in Δ- 6
- $\bullet$ - Succinic in β- 7

1

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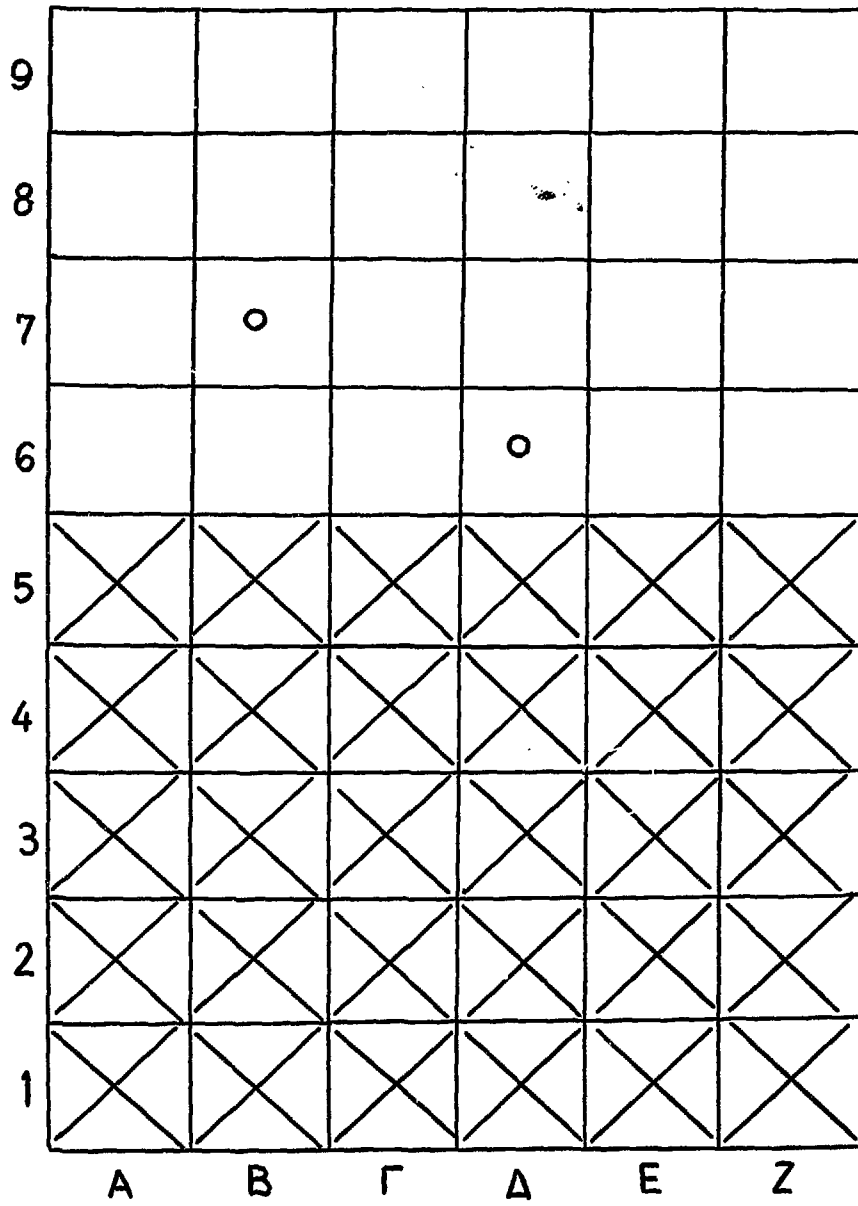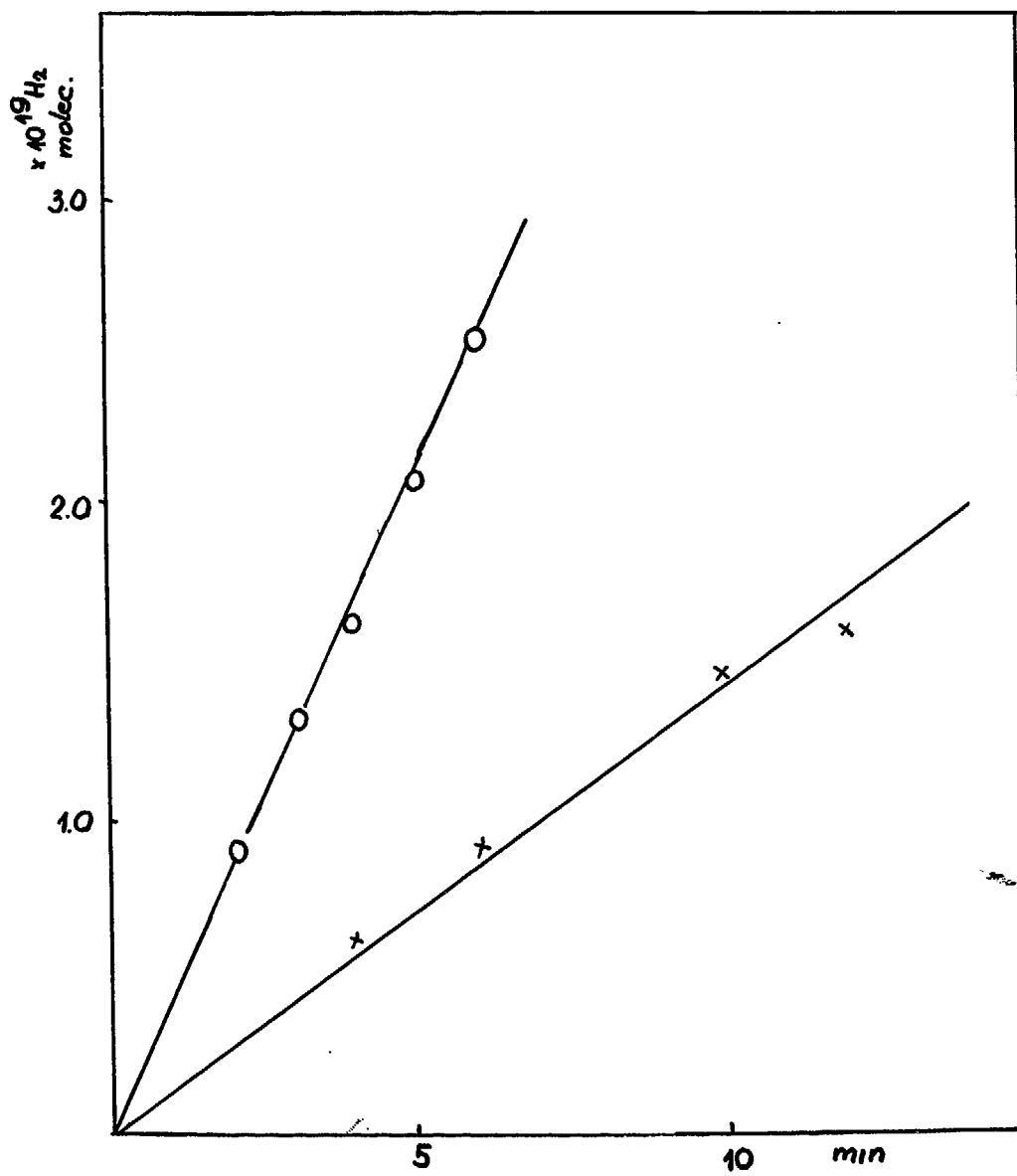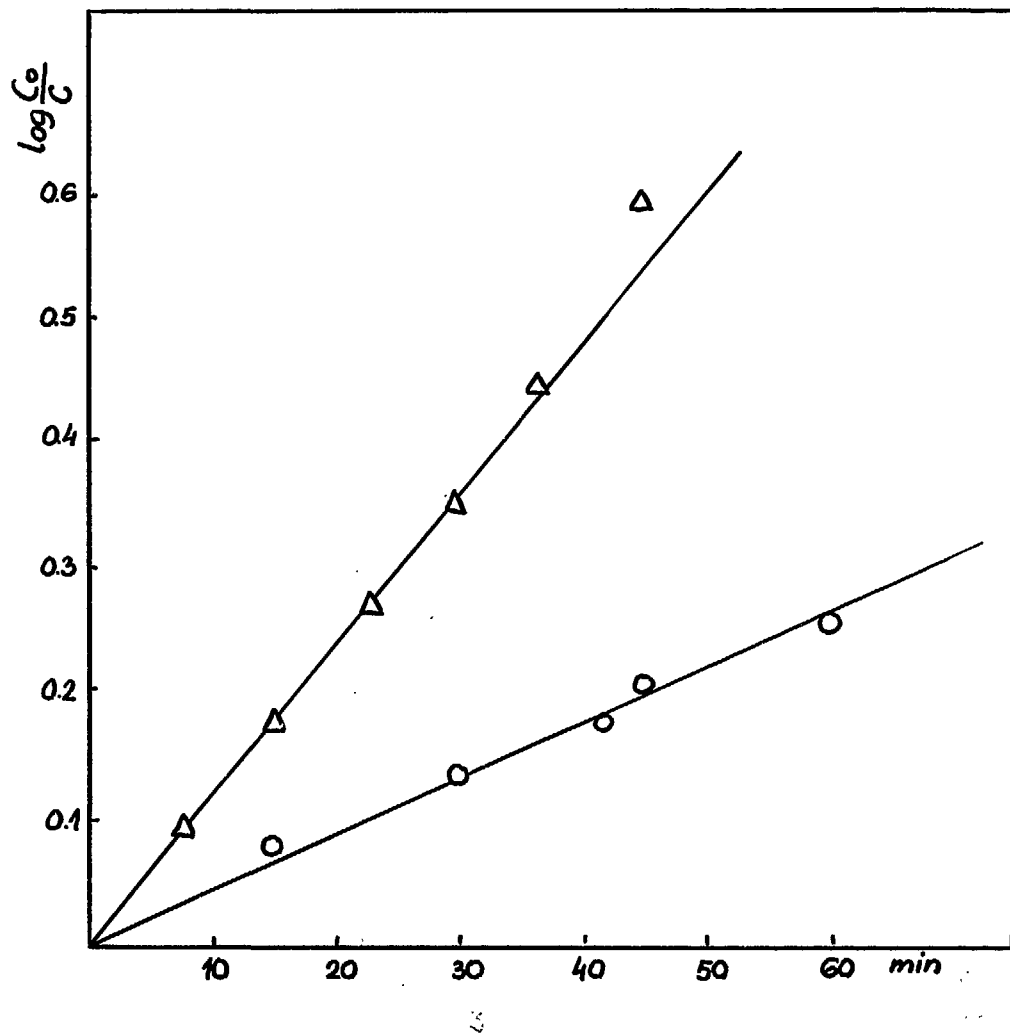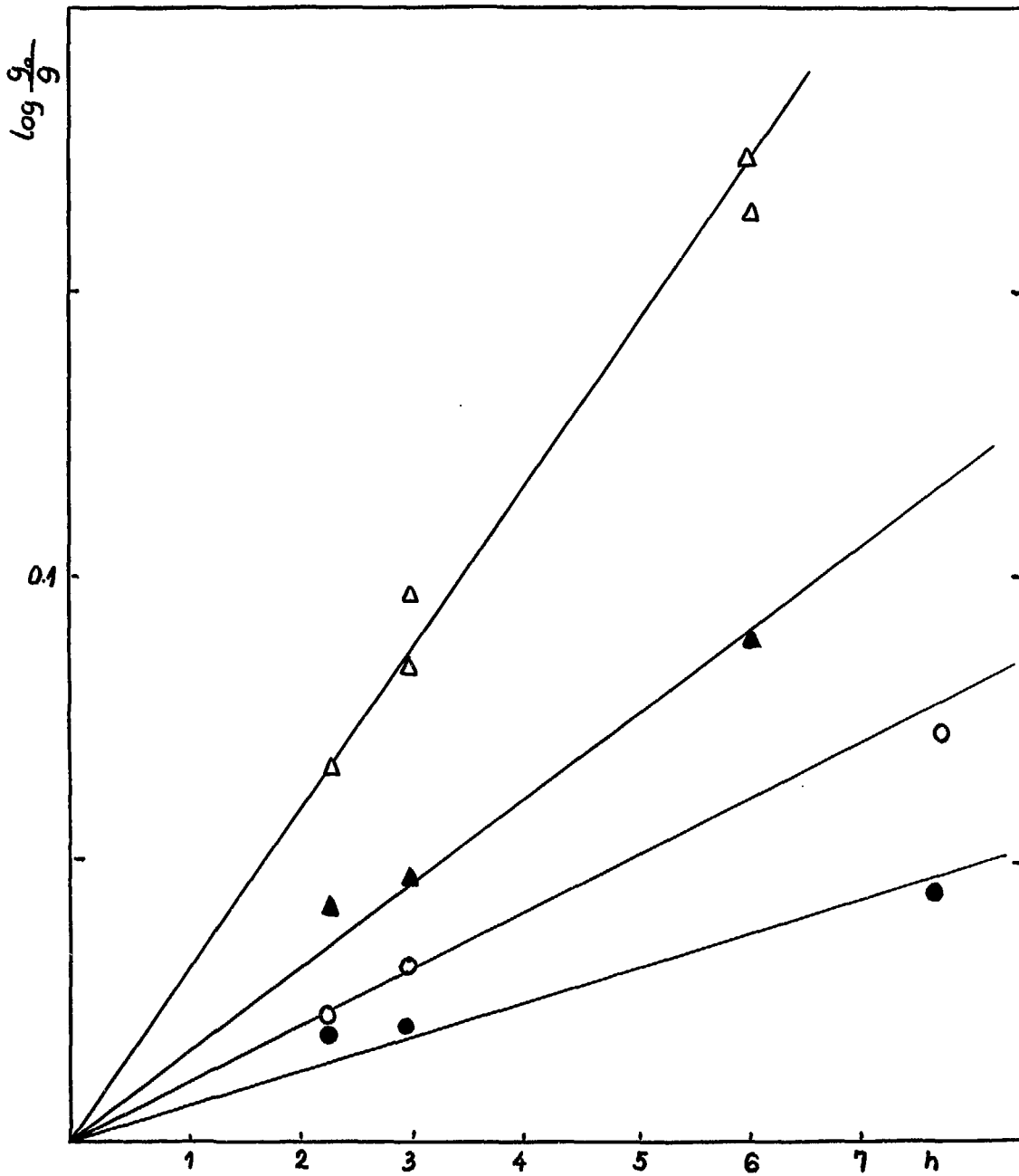
LETTER TO THE EDITOR

INTERCOMPARISON IN-PILE DOSIMETRY IN GRR-1[*].
CALORIMETERS AND CHEMICAL DOSIMETERS: CYCLOHEXANE
AND DICARBOXYLIC ACIDS

There are a number of chemical dosimeters which
have been recommended for in-pile use[1]. However, the
number of systematic studies of their behaviour in diffe-
rent reactor cores is still rather limited[2]. The pre-
sent experiment was undertaken to clarify the discrepan-
cies in the results in the intercomparison experiments
performed so far[3,4,5]. The total dose and the relative
contributions of neutrons and gamma rays were determined
by calorimetric measurements, using a "Vinča" calorime-
ter[3,4,6], with graphite and polyethylene samples. The
fast neutron fluence was measured by Ni-detectors and the
thermal neutrons fluence by the activation of Au-foils.
The chemical systems were cyclohexane, exalic acid solid
and in aqueous solution and solid succinic acid which we-
re irradiated in the same positions as calorimeters. Mea-
surements were made in the GRR-1 reactor[5], in the dry
channels installed in the positions $\Delta - 6$ (4 cm from the
core) and $\beta - 7$ (12 cm from the core) in the reflector.
Reactor power was limited to 1 MW. The preparation and tre-
atment of chemical samples were done as described in re-
ferences[1,7,8,9,10,11].

The neutron flux densities are

Position	$n \ cm^{-2} s^{-1}$	
	Fast	Thermal
$\Delta - 6$	1.95×10^{12}	0.97×10^{13}
$\beta - 7$	0.43×10^{12}	2.93×10^{12}

The contribution of thermal neutrons to the total absorbed dose was estimated to be less than 1% and was neglected[12]. Calorimetric measurements gave the following dose rates

Material	$Mrad \ h^{-1}$	
	$\Delta - 6$	$\beta - 7$
Graphite	49.8	21.8
Polyethylene	90.0	34.5

wherefrom one derives the contributions from neutrons and gamma rays (in $Mrad \ h^{-1}$)

Material	$\Delta - 6$			$\beta - 7$		
	Neutron	Gamma	Total	Neutron	Gamma	Total
Graphite	3.4	46.4	49.8	1.0	20.8	21.8
Polyethylene	37.2	52.8	90.0	10.8	23.7	34.5

The reliability of calorimetric measurements was checked by evaluating the neutron contribution from the measured neutron flux density and comparing is to the corresponding values derived from calorimetry. For polyethylene this was done in several ways as presented below

| Derived by | Mrad h^{-1} | | Reference |
	$\Delta - 6$	$\beta - 7$	
Calorimetric Measurements	37.0	10.8	(1)
ASTM Procedure Fission Spectrum	39.6	8.64	(13)
ASTM Procedure dE/E Spectrum	45.6	9.70	(13)
C.E.A. Method	44.0	9.55	(14)
Combined Method 1MeV Fission Spectrum 1MeV $\frac{dE}{E}$ (E)	44	9.66	(14)
Combined Method dE/E Spectrum	49.3	11.9	(15)

One can see that for the $\Delta - 6$ position a better approach is the one which assumes the fission spectrum, whereas for $\beta - 7$ a better agreement is obtained with a dE/E spectrum. This corresponds to the fact that $\Delta - 6$ is close to the core, whereas $\beta - 7$ is separated from the core by more than 10 cm of water.

The results obtained with chemical systems are presented below. Their usefulness for in-pile measurements in terms of the ratio Obtained/Predicted is also given, where "predicted" means the value derived from calorimetric data for the respective compound

| Position | Mrad h^{-1} | | | |
	Cyclo-hexane	Oxalic Aqueous	Oxalic Solid	Succinic Acid
$\Delta - 6$	110	80.0	56.7	75.4
$\frac{\text{Obtained}}{\text{Predicted}}$	1.20	1.03	0.99	1.30

Continued ......

Position	Mrad h^{-1}			
	Cycle-hexane	Oxalic Aqueous	Oxalic Solid	Succinic Acid
β- 7	35.9	29.8	23.2	31.2
Obtained Predicted	1.05	0.96	0.96	1.28

To summarize:

- Calorimetric values, being checked by fast neutron results, were taken as "standards" for the evaluation of absorbed doses in the dosimeters.

- Cyclohexane, a thoroughly investigated dosimeter has been applied as an in-pile dosimeter in several reactors. The 20% discrepancy in its value in Δ - 6 is surprising and shows that some direct intercomparison measurements (e.g. calorimetry with cyclohexane and polyethylene) are still needed.

- Oxalic acid showed a good agreement this time both as solid and in solution. However, the same systems at the ISIS reactor[3,4] showed considerable deviations,which shows that more combined experiments, as the present one, are advisable.

- Succinic acid showed both now and at ISIS much higher values than these derived from calorimetry. This attractive dosimeter needs more study to obtain an accurate a value.

The work is published in complete details by the Greek Atomic Energy Commission as DEMO Report No 74/8 (1974.)[16].

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B.B. RADAK and   Boris Kidrič Institute of Nuclear Scien-
O.S. GAL   ces, Radiation Chemistry Department, Beo-
                  grad, Yugoslavia.
D.G. MARKETOS   Nuclear Research Center "DEMOCRITOS", Ra-
                  diation Chemistry Laboratory, Aghia Para-
                  skevi -Attikis, Greece.
A.W. BOYD   Chalk River Nuclear Laboratories, Chemis-
                  try and Materials Division, Atomic Energy
                  of Canada Limited, Chalk River, Ontario,
                  Canada.

R e f e r e n c e s

1.- A.W.Boyd (editor), Determination of Absorbed Dose in Reactors, IAEA Technical Reports Series No. 127, Vienna (1971).

2.- Meeting of the IAEA Working Group on Reactor Radiation Measurements, Grenoble, France (1970).

3.- B.Radak, O.Gal, V.Marković, Lj.Petković, M.Labrousse, J. Libmann and J. Roger, Nucl.Appl.&Technology, 7, 409 (1969).

4.- M.Labrousse, J.Libmann, J.Roger, B.Radak, O.Gal, V.Marković and Lj.Petković, C E A – N – 1168 (1969).

5.- D.G.Marketos and A.W.Boyd (editors), International Intercomparison of Chemical Dosimeters for In-Pile Use, Greek Atomic Energy Commission, Nuclear Research Center "Democritos" Report DEMO 74/5 (1974).

6.- A.W.Boyd (editor), International Intercomparison of Calorimeters, IAEA Technical Reports Series No. 128 (1970).

7.- V.Marković and I.Draganić, Rad.Res., 36, 588 (1968).

8.- O.Gal, Ph.D.Thesis, University of Beograd (1967).

9.- O.S.Gal and I.G.Draganić, Int.J.Appl.Rad. and Isotopes, 22, 753 (1971).

10.- A.W.Boyd, H.W.Coner and J.J.Pieroni, CRNL Report AECL-2203 (1965).

11.-O.Gal and P.Premović, Int.J.Appl.Rad.and Isotopes, 23, 541 (1972).

12.- J.K.Linacre, C.R.V.Reed, N.K.Taylor and R.B.Thomas, AERE-R 4807 (1965).

13.- ASTM Standards, Annual Book, Part 27 (1970).

14.- P.Mas and Y.Dreulers, Raport C E A - R 2510 (1964).

15.- B.Radak, Ph.D.Thesis, University of Beograd (1964).

16.- B.B.Radak, O.S.Gal, D.G.Marketos and A.W.Boyd, Intercomparison of Dicarboxylic Acids, Cyclohexane Dosimeters and Calorimeters in the Greek Research Reactor - November 1973., Greek Atomic Energy Commission, Nuclear Research Center "Democritos", Report, DEMO 74/8 (1974).

DECOMPOSITION OF SOLID OXALIC ACID BY HEAVY CHARGED PARTICLES
from the ^{6}Li(n, alpha)^{3}H REACTION

by

O.S. GAL and B.B. RADAK,
"Boris Kidrič" Institute of Nuclear Sciences - Vinča,
Beograd, Yugoslavia

Radiolytic behaviour of solid oxalic acid has been
studied in a number of publications and the results were re-
cently reviewed[1]. In these investigations particular atten-
tion has been paid to the possibility of dosimetric applica-
tion of this system both in gamma and mixed radiation field
in nuclear reactor. As a results the radiolytic yields of the
stable products as well as some plausible suppositions on the
reaction kinetics came out of these studies. Although   some
quantitative differences ("sensitivity" to different kinds of
radiation) were observed, it was pointed out that the decom-
position process was the same with both kinds of radiation.
It was concluded that the differences originated from the
presence of the neutron component in the mixed pile radiati-
on.

In order to make the differences of radiolytic ac-
tion of different kinds of radiation "clearly visible", in
the present work the decomposition produced in solid oxalic
acid by heavy particles from ^{6}Li(n, alpha)^{3}H reaction was me-
asured and the results compared with those ones produced by
pure gamma radiation.

Mixtures of solid oxalic acid with lithium oxalate

having different molar fractions were irradiated by thermal neutrons in the present work. The remarkable difference of these two compounds, regarding their response to the radiation[2,3], made it possible to determine the decomposition of oxalic acid itself. Moreover, it was possible to determine its decomposition caused by the products of $^6Li(n, alpha)^3H$ reaction only, provided that thermal neutrons do not produce any radiolytic change in oxalic acid, and its decomposition due to the small fraction of gamma radiation in experimental channels, was determined by irradiation of the pure oxalic acid at the place. There was an uncertainty of the effectivness of energy created in lithium oxalate, i.e., of its action to the intimately, but still mechanically, admixed oxalic acid. Therefore the determination of absorbed doses as well as the grain and sample size effects were an important part of the present study.

The yields of decomposition of oxalic acid and of the CO_2 formation in irradiated samples were determined. Irradiations were performed in graphite reflector of the RA reactor at Vinča.

Experimental

Composition of samples. For most irradiations Merck analytical grade oxalic acid dihydrate and BDH reagent grade lithium oxalate were used without further purification. The ^6Li abundance was proved to be 7.5 atomic per cent by mass spectrometry. In all cases the mole fractions of 0.00, 0.15, 0.25, 0.40, 0.50, 0.60, 0.75, 0.85 and 1.00 of lithium oxala-

te in oxalic acid were prepared. The weighed amounts were
mixed and homogenized in two ways:

a) mechanically, either by hand grinding in a
mortar to the grain size of maximum 20 μ or by vibrator
mill with balls to the grain size of 10 μ maximum, and

b) by freeze-drying of their aqueous solutions
with a grain size of 1 - 3 μ.

The dry product of the latter procedure were let
in air to absorb water and form the dihydrate of oxalic acid.
The compositions of mixtures were checked by permanganomet-
ric titrations for the oxalate ions and by a gravimetric me-
thod with sulfuric acid for Li atoms[4].

The anhydrous form of oxalic acid was also used.
The mixtures to be irradiated were made in the similar way
as it was in the case of the dihydrate form (Procedure a).
The crystalline anhydrous form was prepared by sublimation
of the dehydrated oxalic acid in vacuo at ca. $120^{\circ}C$.

Irradiation of samples. For irradiation the ali-
quots of 100 - 400 mg of each mixture were prepared. The
irradiation periods varied from 1 to 4 hours in the experi-
ments for determinations of CO_2 formation and from 1 to 7
hours for the oxalic acid decomposition measurements. The
sealed quarz ampoules (10 mm diameter, 30 mm high) with the
samples were placed into Al can and irradiated together with
the weighed Co metal wires for monitoring the thermal neut-
ron fluence. The thermal neutron flux density, $\emptyset_{th}$, at this
location was $1,25 \times 10^{12} n \ cm^{-2} s^{-1}$ with reactor operating at
500 kW at which power all irradiations were performed. In a

separate experiment it was shown that the temperature in the bulk of lithium oxalate samples did not exceed 50°C. The gamma ray dose rate was measured by the aqueous oxalic dosimeter[5] and the average of many determinations gave a value of 0.5 Mrad h^{-1} at the irradiation conditions.

Analysis. Decomposition of oxalic acid was measured by determinations of the loss of oxalic ions after irradiation. The irradiated and ... samples were dissolved in water and the total oxalate content was determined by permanganometric titration[6]. Paralell samples were analysed for CO_2 formation by gas-chromatography[2]. Before analysing the irradiated ampoules were heated for one hour at 94°C.

Corrections. Chemical effect of gamma radiation in solid oxalic acid and self-decomposition of lithium oxalate were determined in each set of irradiations. The samples of pure oxalic acid (mole fraction 0.00) and of pure lithium oxalate (mole fraction 1.00) were irradiated together with other samples and subsequently analysed in the same way for CO_2 formation and the loss of oxalate ions. These corrections amounted to a few per cent of the total decomposition in the mixed samples.

Dosimetry. The radiation energy absorbed per mole of solid oxalic acid from the ^{6}Li fission recoil particles is expressed as

$$D \text{ (eV mole}^{-1}) = \phi_{th} \, t \, \acute{6} \, N \, E_f \, n_{Liox} \, \frac{f_{(Z/A)}}{n_{ox.acid}} \qquad (1)$$

where

$$\phi_{th} \, t \, \acute{6} \, N \, E_f \, n_{Liox} = D_{tot} \text{ (eV)}$$

is the total energy released by ^{6}Li fission in the irradia-
ted sample; $\emptyset_{th}$ is the thermal neutron flux density, t the
irradiation time in seconds, σ' the neutron capture cross
section of ^{6}Li (945 barns), N the number of ^{6}Li atoms in one
mole of lithium oxalate using the natural isotopic abundan-
ce of ^{6}Li (0.075), E_f is the total energy released per ^{6}Li
fission (4.787 MeV). This total energy is assumed to be com-
pletely absorbed by the sample because of the short range of
the recoil particles and small grain-size of lithium oxala-
te. The self-shielding corrections for neutrons were negle-
cted because of the small ^{6}Li content even in the samples
with the largest ratio of lithium oxalate to oxalic acid. The
quantity n_{Liox} is the number of moles of lithium oxalate in
the particular sample. The fraction $f_{(Z/A)}/n_{ox.acid}$ in expre-
ssion (1) relates to the part of the total energy released
from Li-oxalate which is absorbed by the solid oxalic acid
present in the mixture, given per mole of the latter. $f_{(Z/A)}$
is the ratio of electron density of oxalic acid to the same
value of the irradiated mixture. This factor is assumed here
to be a good approximation for correction although it is st-
rictly valid for higher energies[7]. $n_{ox.acid}$ is the number
of moles of solid oxalic acid in the sample.

Calorimetric dosimetry. In order to get the direct
value of the energy created by neutrons in lithium oxalate at
the irradiation place, a differential calorimetric measurement
was made. The standard "Vinča" calorimeters[8] were used in
such a way that the "empty" body was graphite-in-alumunum,
whereas the active body was of the same composition plus a
known amount of lithium oxalate. Calorimetric measurements
were performed at two places: one for irradiation of chemical

samples and the other for monitoring of chemical irradiations.

Assuming that in the graphite reflector only the thermal neutrons are present the following value for te flux density is obtained

$$\emptyset_{th} = 1.15 \times 10^{12} \ n \ cm^{-2} s^{-1}$$

which agrees with our earlier measurements[2] i.e. $1.23 \times 10^{12} n \ cm^{-1} s^{-1}$.

Neu_tr_on f_lux_determin_ation_s. Thermal neutron flux density at the irradiation place was determined from the activity of the weighed pieces (about 5 mg) of cobalt wire attached to each group of irradiated samples. During past two years about 50 pieces of wire were exposed and measured from which a mean value of

$$\emptyset_{th} = 1.05 \times 10^{12} n \ cm^{-2} s^{-1}$$

was derived. The standard deviation of each single series was 8 - 9%. This agrees reasonably with the above value derived from calorimetry.

Results and Discussions

Results of three series of measurements are presented in Fig. 1 (lower line). It is a plot of net, i.e. caused by $^6Li(n, \ alpha)^3H$ reaction only, decomposition rate of oxalic acid dihydrate against the absorbed dose. Logarithmic plot is used because the decomposition of oxalic acid is a first

order process in other radiation fields[9]. The abscissa is
obtained from the thermal neutron flux density data and the
respective mole fraction of lithium oxalate in the samples.
There are 7 - 10 values of both abscissae and ordinates for
each of the points in the diagram, showing a standard devia-
tion of 8 to 9%. The upper line presents the results of one
single irradiation series in which the simultaneous calori-
metric measurements also showed the increased values. This
indicates a higher neutron flux density which corresponds to
the fact that the irradiation was made just before the ex-
change of the reactor fuel. The linearity of the decomposi-
tion shows that there are neither the rate (up to 2×10^{24} eV
$M^{-1} h^{-1}$) nor the total absorbed dose (up to 1.5×10^{25} eV M^{-1})
effect.

In Fig. 2 the results for the CO_2 formation are
presented against the same abscissa.

From Figures 1 and 2 one derives the following G-
-values

$$G(-Ox) = 2.6$$
$$G(CO_2) = 5.0$$

which is in a logical agreement one with another, pointing
out that the decomposition of one oxalate gives nearly two
CO_2 molecules.

Since these G values are rather low, their relia-
bility deserves a particular attention. The limits of error
of both abscissae and ordinates are relativly high, which is
familiar with such in-pile measurements. This however can not

explain the obtained G values which are nearly two times lower than those for gamma rays. Therefore the retention of the energy generated within the grains of Li-oxalate, i.e., its availability for the reactions in the grains of oxalic acid, is more carefully considered.

Grain size and the useful particle energy.

If a continuous medium of $Li_2C_2O_4$ is placed in the thermal neutron flux, every point can be a source of alpha particles. The energy of the particles emerging from the point O_1 (Fig. 3) is totally absorbed within a circular area having a radius equal to the particle range. The same is valid for any other point, e.g. O_2. If the absorption is linear with the range, the fraction of energy dissipated from the point O_2 and absorbed within the first circle, O_1, will be proportional to the shadowed area over the area of the circle. The same is valid for the real, three-dimensional case. If the grain size of interest is equal to the doubled particle range, we will consider only the points within the sphere of radius R (Fig. 4). The probability, $\mathcal{P}a$, of absorption of particle is proportional to the doubled volume, V (2), of spheric segments over $\overline{AB}$, divided by the volume of the sphere itself

$$\mathcal{P}_a(r) = \frac{V(r)}{Vo} \tag{1}$$

If we denote $r = \overline{O_1 O_2}$

and take

$$V_{segment} = \frac{1}{3} \mathcal{J} h^2 (3R-h) \tag{2}$$

where

$$h = R - \frac{r}{2} \tag{3}$$

we can find

$$\rho_a(r) = 1 - \frac{3}{4}\left(\frac{r}{R}\right) + \left(\frac{1}{16}\right)\frac{r}{R}^3 \qquad (4)$$

Let there are n_o alpha particles generated per unit volume, and let each of them has an energy E_o. Within the sphere having R = particle range we choose a volume element, dV, from which the total energy $n_o E_o$dV emergres. From this energy an amount

$$dE_{abs} = n_o E_o \, \rho_a(r)dV \qquad (5)$$

will be absorbed within the sphere. The absorbed fraction of the total energy produced in the sphere is

$$\frac{E_{absorbed}}{E_{produced}} = \frac{\int\limits_o^V n_o E_o \rho_a(r)dV}{\int\limits_o^V n_o E_o dV} = \frac{3\int\limits_o^R \rho_a(r)r^2 dr}{R^3} \qquad (6)$$

Combining the equations (4) and (6) one obtains

$$\frac{E_{absorbed}}{E_{produced}} = 0.47$$

Under the given conditions (R=particle range) about a half of the energy is absorbed within the grain. As stated at the begining the maximum grain size was 20 microns, i.e. about twice the particle range[10], to which the derived fraction of the retained energy (0.47) corresponds. However, most frequent were the sizes between 5 and 10 microns in mechanically homogenized mixtures, in which the retention is estimated to between 2 and 10 per cent. On the other hand, the fast tritons, carrying

the other half of the energy of nuclear reaction, have a considerably longer range. One may therefore conclude that the influence of the grain size was in our cases of minor importance.

This conclusion is in agreement with the results obtained with the freeze-dried samples i.e., no difference was observed between their decomposition and the one we found with mechanically homogenized samples.

It was also supposed the energy released was not totally absorbed within the small sample of 100 to 400 mg. A series of 1 g samples for all molar ratios was then irradiated. The results agreed with the smaller samples within the limits of experimental error.

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REFERENCES

1. I.G. Draganić and O. Gal, Radiation Res. Rev., 3, 167 (1971).

2. O. Gal and B. Radak, Intern. J. Radiat. Phys.Chem., 3, 221 (1971).

3. J. Okamoto, J. Nucl. Sci. Technology, 7, 306 (1970).

4. N.H. Furman (ed.), ScoH's Standard Methods of Chemical Analysis, Van Nostrand Co. Inc. London, 1948., p. 888.

5. V. Marković and I, Draganić, Rad. Res., 35, 587 (1968).

6. O. Gal, Anal. chim. Acta, 49, 370 (1970).

7. (F.H. Attix and W.C. Roesch eds.) Radiation Dosimetry, II part, Academic, New York (1966).

8. B. Radak, O. Gal, Lj. Petković, M. Labrousse, J. Libmann and J. Roger, Nucl. Appl. and Technology, 7, 409 (1969).

9. O. Gal, Lj. Petković, Lj. Josimović, I. Draganić, Intern. J. Appl. Radiat. Isotopes, 19, 645 (1968).

10. S.V. Starodubeev and A.M. Romanov, The Passage of Charged Particles through Matter, ANUSSR, Taskent (1962).

Fig. 1. Decomposition of oxalic acid induced ba the heavy
particles from ^{6}Li(n, alpha)^{3}H reaction.

Fig. 2. CO_2 formation.

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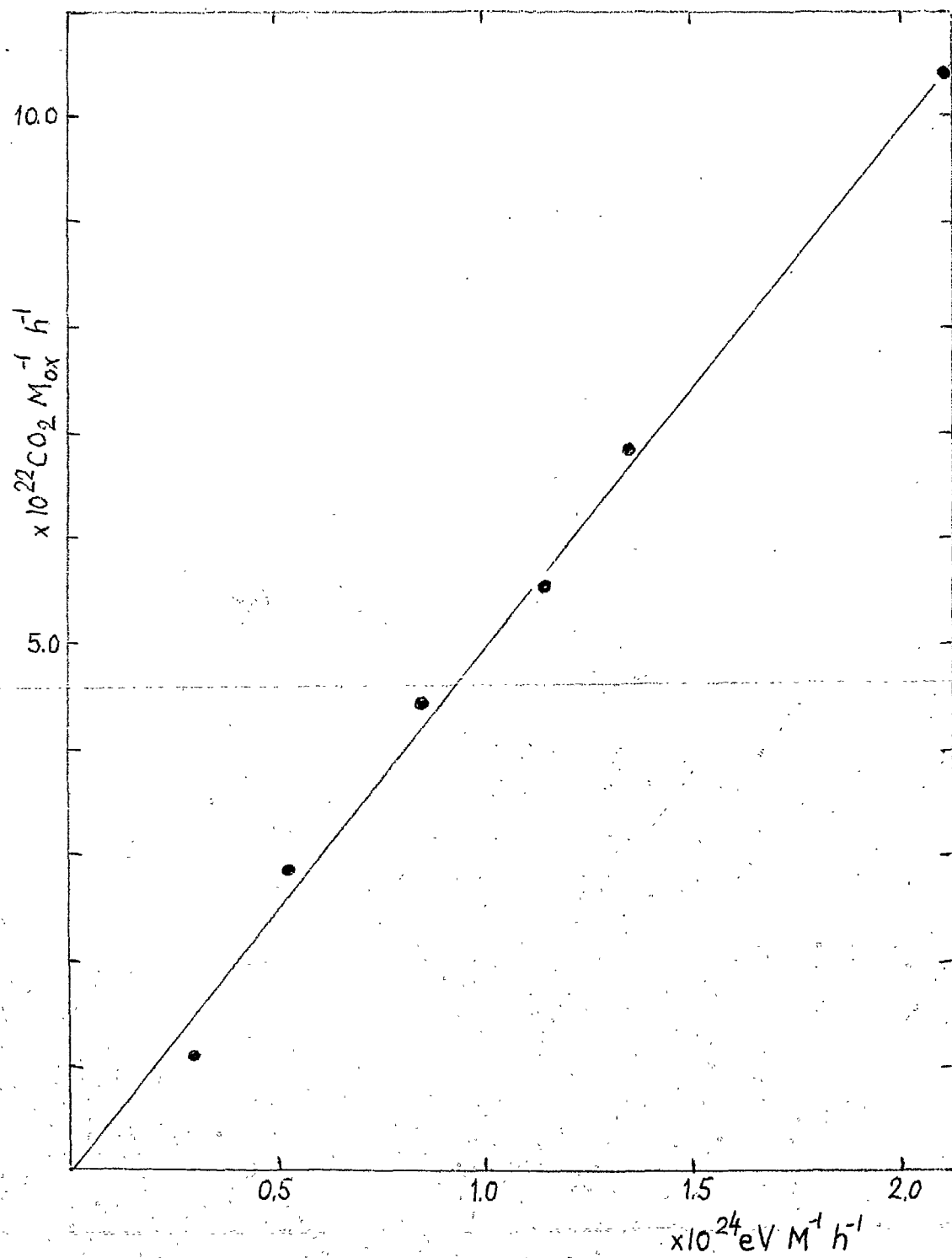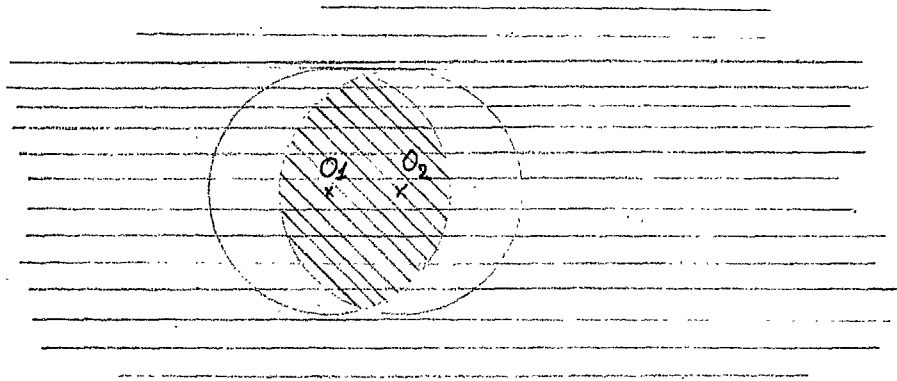mann

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Fig. 1
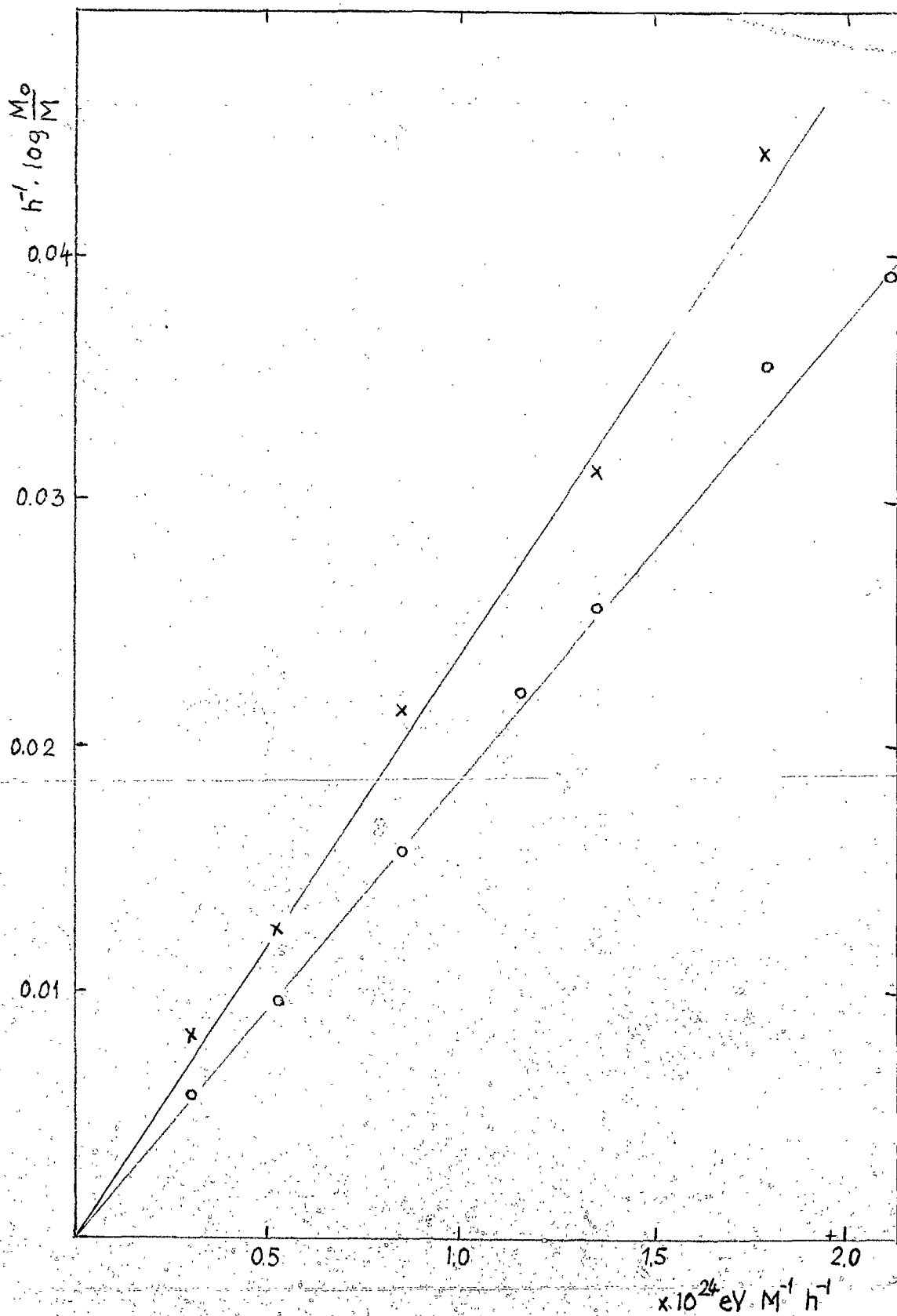
Fig. 2

Fig. 3. Generation and absorption of
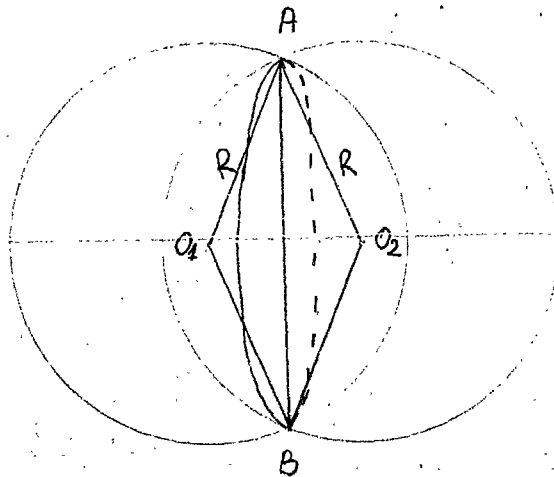monoenergetic alpha particles;
two-dimensional case.

Fig. 4. Self absorption of charged
particles generated within
a grain with the size of par-
ticle range. Three-dimensi-
onal case.