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PREPARATION OF HIGH SPECIFIC ACTIVITY OF ^{51}Cr BY THE SZILARD-CHALMERS EFFECT ON POTASSIUM CHROMATE

by

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1. INTRODUCTION:

The ^{51}Cr is a radioisotope with a half-life of 27.8 days, which decays by K-capture emitting 0,32 Mev gamma rays within 9 per cent of the desintegrations. This radioisotope is generally obtained by radioactivation in a nuclear reactor and it is mainly supplied for biological and medical uses.

Since chromium compounds are toxic, in order to prevent them from being harmful to the patient, the ^{51}Cr solutions intended for the above mentioned uses must be of high specific activity, at least of 10 curies/gram.

Unfortunately, ^{51}Cr of that quality it is not feasible to be obtained by means of the straightforward radioactivation reaction, $^{50}Cr(n, \gamma)^{51}Cr$, taking place on natural chromium compounds. Only in the very special cases of using high thermal flux densities and ^{50}Cr enriched targets, it is possible to reach the specific activity required by simple irradiation (1).

The ^{51}Cr of high specific activity is usually obtained by applying the Szilard-Chalmers reaction principle to specially chosen chromium compounds, in which the chemical effects accompanying the (n, γ) reaction enable the separation of a fraction of the ^{51}Cr formed with specific activity about one thousand times more than that of the unprocessed target (1, 2, 3, 4, 5, 6, 7, 8, 9, 10).

The potassium chromate is by far the most frequently used

target material for the production of ^{51}Cr by the Szilard-Chalmers process. Other compounds, however, have been tried with this aim: The Palatine Fast Blue GGN (5), the chromium acetylacetonate (7), the chromium oxinate (11), the ammonium dicromate (7, 14), the chromic oxide (8), etc., but in all the cases the potassium chromate has shown to be superior for high neutron fluency.

On irradiating the potassium chromate, some of the ^{51}Cr formed by the reaction $^{50}Cr(n, \gamma)^{51}Cr$ appears in the trivalent state. These chromium ions may then be separated from the irradiated bulk of chromate by several methods: by precipitation as hydroxide (6), by coprecipitation with aluminium hydroxide (4) (10), by absorption of the chromate ions on an anion exchange resin (8), by the selective uptaking of the trivalent chromium on an alumina column (9), etc. We have chosen, because of its simplicity, the separation method of the chromium hydroxide precipitation.

2. EXPERIMENTAL

Target. - 100 gram of potassium chromate Mallinckrodt, p. a.

Container. - Water-tight aluminium can.

Irradiation facilities. - The irradiation basket in the I-5 possition of the swimming-pool reactor JEN-1, (13).

Irradiation flux density. - 1.9×10^{12} neutron/cm^2/seg, at 1 Mwatt

Neutron Fluency. - That of an integral number of weeks at 20 Mwatts x x hour/week. During the shutdown intervals the samples remained in the reactor core.

Apparatus. - That of the scheme in Fig. 1.

Cooling time. - About 4 days from the shutdown.

Biological protection. - A wall 5 centimeter thick of lead bricks.

2.1. Separation Method

1 - the irradiated target (100 gram) is dissolved in 250 ml of water. The solution is allowed to rest for at least 4 hours.

2 - the chromium hydroxide settled during that time is separated by filtering through a No. 4 sintered glass plate. The chromate ions are rinsed down and the retained precipitate is washed throughout by 250 milliliters of water.

3 - the water-washed precipitate is dissolved in 5 milliliter of 10 per cent hydrocloric acid by gentle heating, and it is again reprecipitate by neutralizing the solution to the phenolphtaleine red with 10 per cent ammonium hydroxide.

4 - the chromium hydroxide once filtered and washed is oxidized to chromate by 1 milliliter of Perhydrol and 5 milliliters of 0.1 M sodium hydroxide. The excess of oxidizing agent is destroyed by boiling.

5 - the chromate solution is made isotonic saline by adding 1 milliliter of 1:5 diluted phosphoric acid and further adjustment of the pH value to 7 with 1 M sodium hydroxide. The solution is finally made up with water to 10 milliliter volume.

3. DISCUSSION OF RESULTS.

The preparation of ^{51}Cr of high specific activity has been considered here to depend mainly on two factors:

a) the goodness of the separation of Cr^{3+} and CrO_4^{2-} ions.
b) the length of the irradiation time.

The separation of Cr^{3} and CrO_4^{2-} ions from each other is accomplished by retaining the chromium hydroxide precipitate on a sintered glass plate and washing it throughout with water. In order to determine the effectiveness of the washing to eliminate the CrO_4^{2-} ions which remain adsorbed or occluded by the precipitate, the specific activity of the successive fractions of water filtering through was analyzed. It was found, Fig. 2, that the specific activity of the fractions rises steeply during the first 100 milliliter, but with further washing it tends to a constant value, which is actually lower than that of the washed precipitate. From that, it can be inferred that prolonged washing with water desorbes only very slowly the chromate ions; therefore, a reprecipitation of the chromium hydroxide seemed to be advisable. In fact, the reprecipitation step can improve the specific activity of the product by a factor of 10 per cent or more.

The specific activity of a radioisotope prepared by a Szilard-Chalmers process depends on all those factors which yield the element in the target to the chemical state in which appear the radioactive atoms that separate in the enriched fraction.

The quantity of element accompanying the enriched fraction can be considered to arise from two different sources: that existing in the material before the irradiation took place, and that produced in it be-

cause of the radiolytic damage undergone during or after the irradiation. In steady irradiation conditions, it will be assumed this second source to be lineally dependent on the time (12). So, for one gram of irradiated material, the quantity of element separated can be expressed as, (see Table 1):

$$G = G_0 t + C \qquad 3.1.$$

If we accept, furthermore, that the retention, R, can be taken as a constant for any irradiation time, the following expressions will hold:

$$Q = S\,(1 - e^{-\lambda t}) \qquad 3.2.$$

$$A = (1 - R)\,S(1 - e^{-\lambda t}) \qquad 3.3.$$

$$E = \frac{(1 - R)\,S(1 - e^{-\lambda t})}{G_o t + C} \qquad 3.4.$$

$$F = \frac{1 - R}{G_o t + C} \qquad 3.5.$$

Where S represents the average saturation specific activity of the target in the irration position. The meaning and units of each symbol used are summarized in Table I.

According to equation 3.4 the specific activity of the enriched fraction will be strongly dependent on the irradiation time and, therefore, careful attention should be paid to the length of the irradiation. Actually, the specific activity is not the only important factor in a Szilard-Chalmers process. It may be shown that what best represents it, from the point of view of the radioisotope producer, is an index which takes into account the amount of activity separated in the enriched fraction from one gram of irradiated material, and the time during which its specific activity is greater than the threshold value U accepted for the medical or biological uses of this radioisotope. This index may be quantitatively defined as:

$$P\ (\text{mc} \times \text{day}) = \frac{A(\text{mc})}{\lambda(\text{day}^{-1})} \ln \frac{E}{U} \qquad 3.6.$$

where P is implicitly dependent on the time, as can be seen from equations 3.3. and 3.4.

The experimental data of the specific activity found in a set of samples irradiated for an increasing number of weeks have been represented in fig. 3, altogether with their theoretical curves from equation 3.4. These curves have been drawn for reasonable values of the constants involved, special attention being paid to the effect of the amount of trivalent chromium originally present in the sample, for which two values of 0 and 5 μg of trivalent chromium per gram of hexavalent target element have been considered. It should be noted that for short irradiation times, the experimental curve is fairly well described by the theoretical one corresponding to a target biased with 5 μg of trivalent chromium per gram of target element. No direct and conclusive support, however, has been afforded to this point because of the analytical difficulties encountered.

In fig. 4 it can be seen also, that the actual values found for the production index are lower than expected from equation 3.6. when the calculated values of E and A from fig. 3 are used. The maximum in both the theoretical and experimental curves, however, are well positioned and allow to select a narrow zone around three weeks of irradiation time for which the best results from the producer point of view should be expected.

We do not belive, of course, that this simple theory will describe exactly the time dependance of the specific activity and related factors, but we find it helpful to introduce the index P, the time dependame of which allows the experimental determination of the optimum length of the irradiation in a nuclear reactor for the preparation of high specific activity ^{51}Cr by the Szilard-Chalmers process.

TABLE 1: Meaning of symbols used

Symbol	Meaning	Unit
G	Total element separated	gram
G_o	Element dayly yield	gram/day
t	Steady irradiation time	day
C	Originally separable element	gram
Q	Specific activity of irradiated target.	millicurie/gram
S	Average saturation activity	millicurie/gram
	Desintegration constant	day^{-1}
A	Amount of activity separated	millicurie
R	Retention	$(\%).10^{-2}$
E	Specific activity of the enriched fraction	millicurie/gram
F	Enrichment factor	
P	Production index	millicurie.day
U	Threshold accepted for the specific activity	millicurie/gram

Acknowledgment

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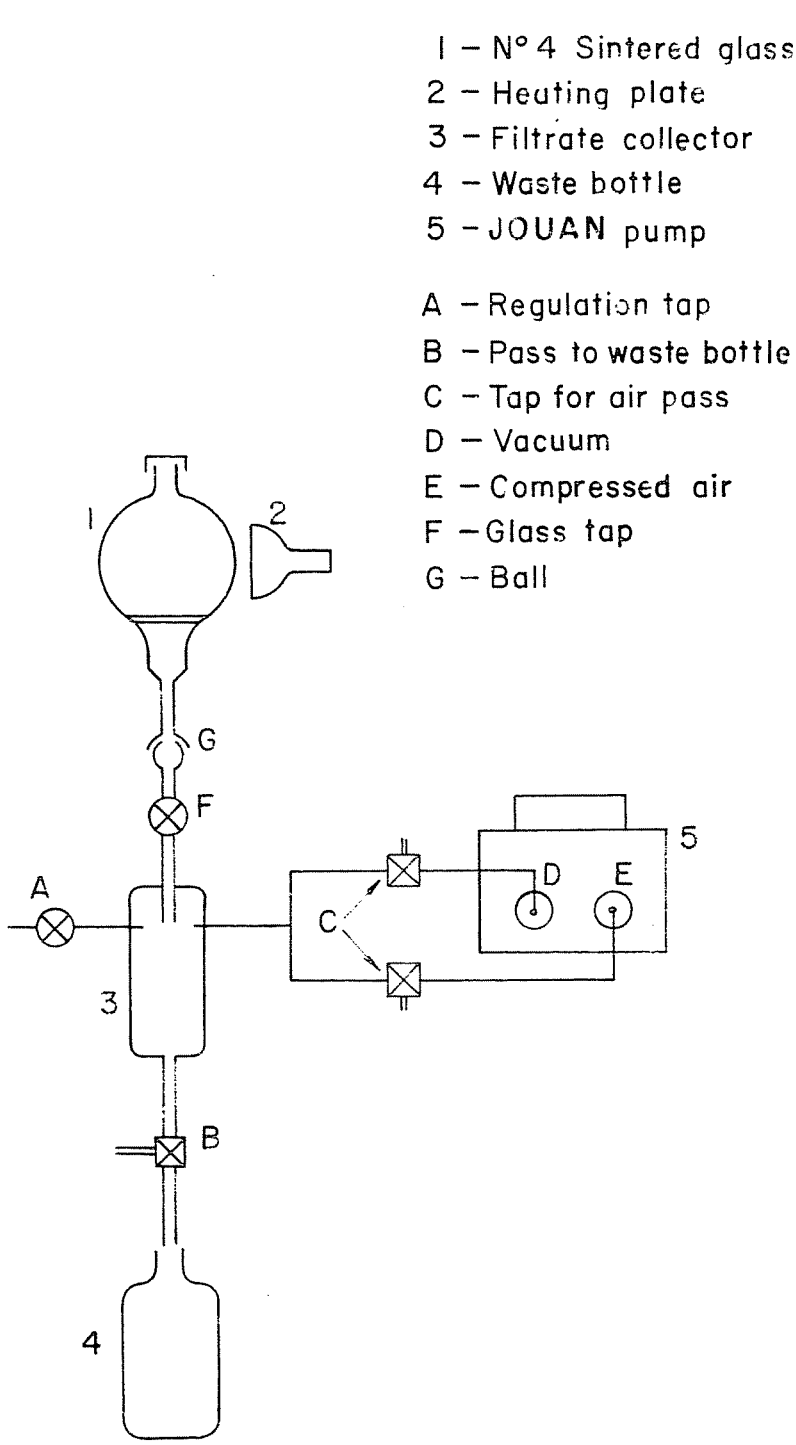

Fig. 1. – Scheme of the apparatus for the obtention of High specific activity ^{51}Cr.

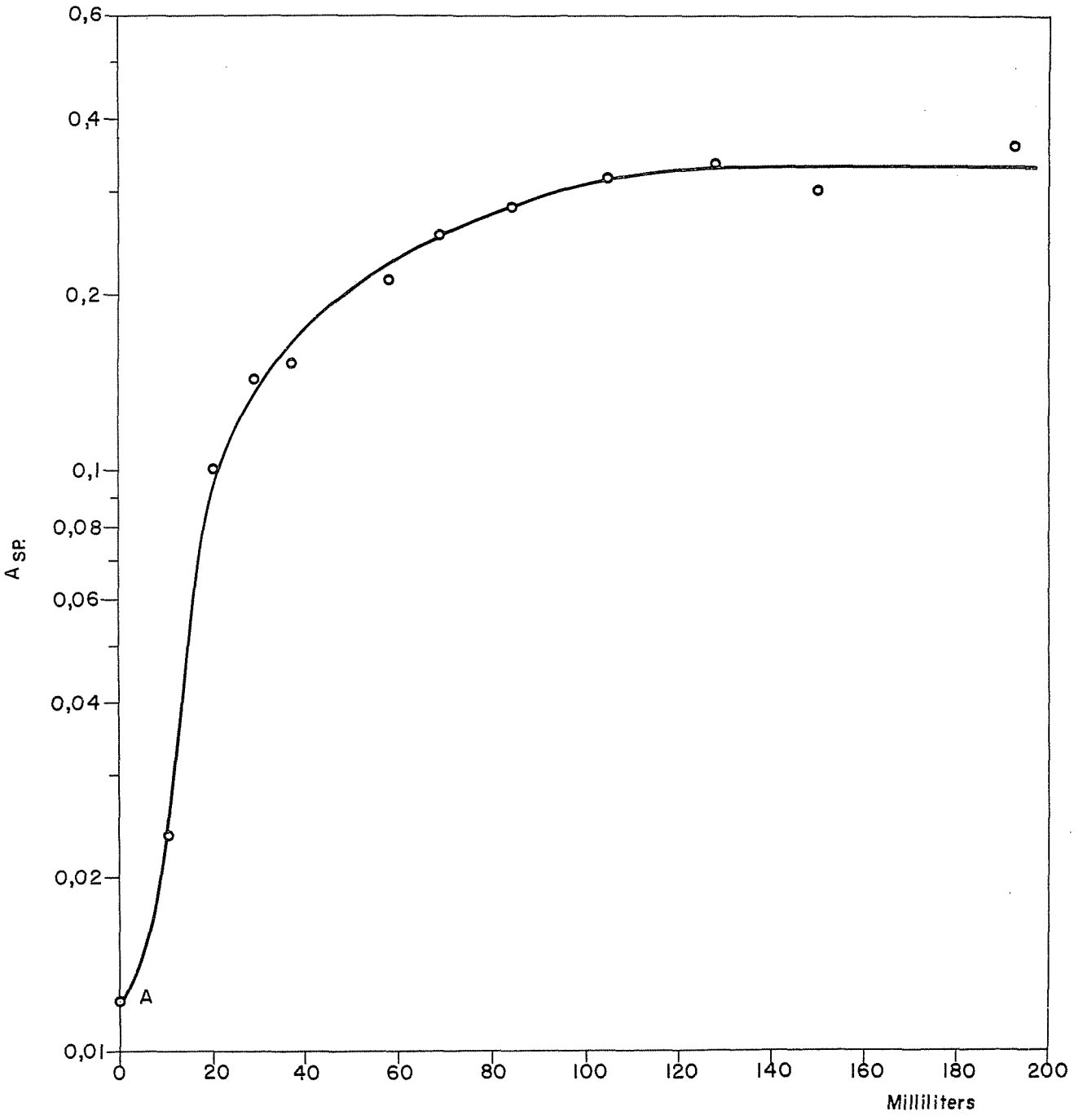

Fig. 2. — Specific ativity of rinsing water versus volume passed.

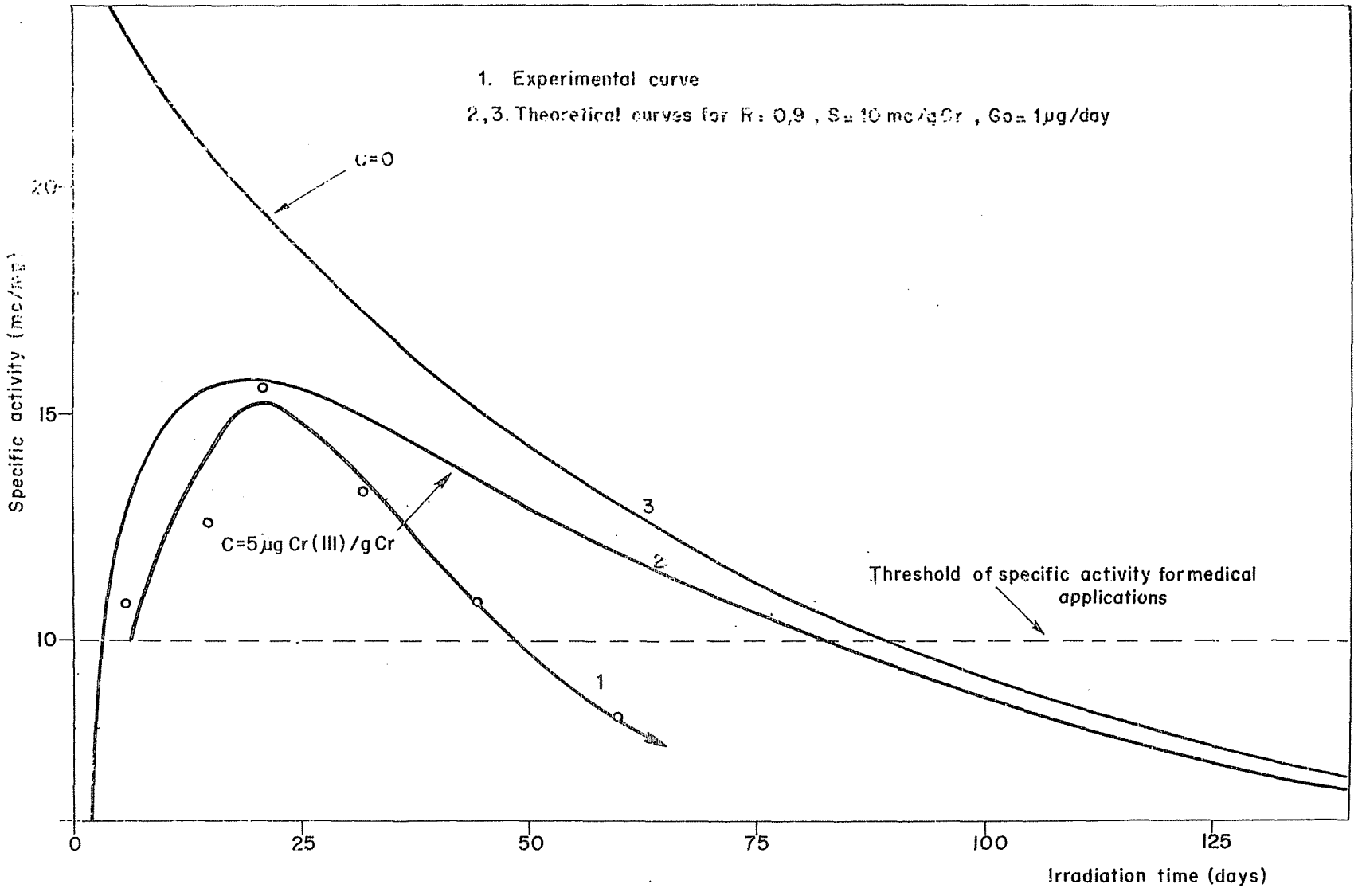

Fig. 3. – Specific activity of separated ^{51}Cr versus irradiation time.

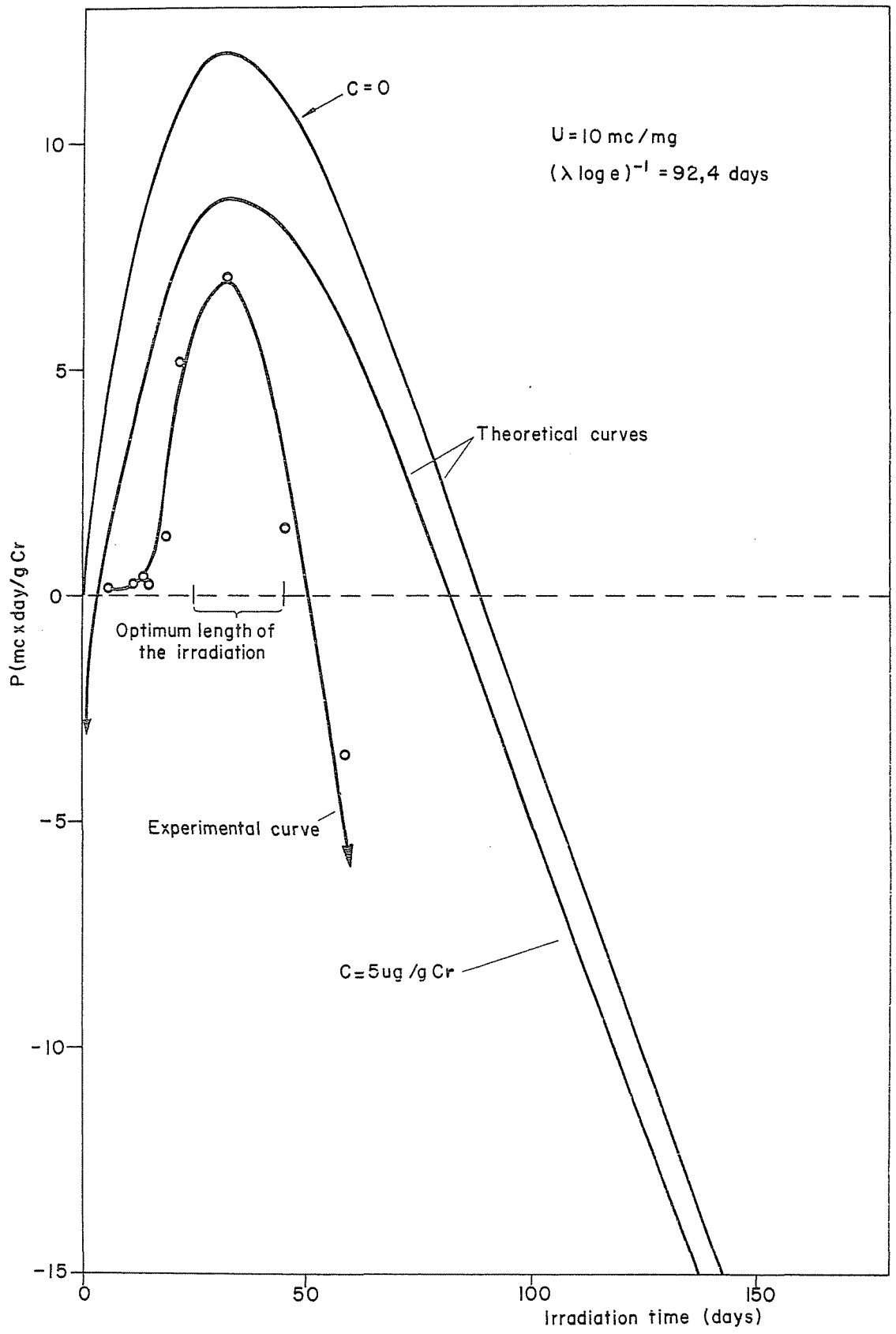

Fig. 4. —Production index versus irradiation time.

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Los iones Cr^{3+}, enriquecidos en ^{51}Cr, que aparecen al poner en solución cromato potásico irradiado con neutrones, son separados como hidróxido de cromo. Los iones $CrO_4^{=}$ ocluídos por el precipitado se eliminan reprecipitando el hidróxido.

La duración óptima de la irradiación, t_o, para la obtención de ^{51}Cr ha sido determinada mediante la posición del máximo en la curva experimental P=f(t),

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en la que el índice P, dependiente del tiempo, se define como el producto del número A de mc de actividad específica E separados por gramo de cromato potásico irradiado, por el número de días durante el cual esta actividad específica es mayor que el umbral U aceptado para usos biológicos. La fórmula que relaciona estos factores es

$$P\ (mc \times día) = \frac{A\ (mc)}{\lambda\ (día^{-1})}\ \ln\ \frac{E}{U}$$

Para una duración de la irradiación de 3 semanas, el método puesto a punto con las facilidades experimentales de irradiación del reactor JEN-1 permite la preparación rutinaria de ^{51}Cr idóneo para aplicaciones médicas.

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